TAMPERE UNIVERSITY OF TECHNOLOGY

TIIA SMOLANDER

STUDY OF POLYPROPYLENE FOR USE IN MOBILE PHONES, AS A FUTURE ECO-FRIENDLY MATERIAL

Master of Science Thesis

Examiners: Professor Minna Kellomäki
and M.Sc. (Engineering) Mika Pelto
Examiners and subject approved in the
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ABSTRACT

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Polypropylene is a thermoplastic mass production plastic, which is currently one of the most commonly used plastics. By chemical structure polypropylene is one of the simplest polymers. The simplicity of the structure affects to rather versatile properties of polypropylene. These versatile and modifiable properties of polypropylene are reason for why it is still of interest to researchers. This Master of Science thesis introduces properties of polypropylene in common level. One of the main goals for this thesis was to study sustainability of polypropylene. The sustainability is studied with Life Cycle Assessment. In a Life Cycle Assessment study energy consumptions and greenhouse gas emissions of polypropylene and some other plastics, which are used in mobile phones, were compared. The thesis also gives an overview of biopolypropylene and biorefinery concepts as well as some possibilities of raw materials of biorefinery are introduced. Also market and industry trends of polypropylene now and in the future are considered. By the end the reader will also have a basic knowledge of materials used in mobile phones in general and more specifically about plastics. In plastics are focused plastic materials which might be replaceable with some a polypropylene plastic. At the moment some amount of polypropylene plastics are used in mobile phones, but not in structural parts like covers or frames. Another main goal of this thesis was to examine if polypropylene plastics could be used more in mobile phones than currently and suitability of their manufacturing methods. This was done by comparing plastics and by testing injection moldability of selected polypropylene plastics. The plastics were chosen to injection moldability test by their mechanical properties. Reference materials were plastic materials whose are currently used in mobile phones. The three selected polypropylene plastics were injection molded to mobile phone cover like test pieces. By these test plastics injection moldability and some of their properties, like shrinking, were studied. After the injection molding test it is clear if the selected plastics could be processed to wanted shapes by injection molding. Test pieces mechanical properties suitability for wanted use was not studied with injection molding tests.

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Polypropeeni on kestomuovi ja se on myös yksi käytetyimmistä muoveista. Kemialliselta rakenteeltaan polypropeeni on yksi yksinkertaisimmista polymeereistä ja tämä suhteellisen yksinkertainen kemiallinen rakenne vaikuttaa polypropeenin monipuolisiin ominaisuuksiin. Nämä monipuoliset muunneltavat ominaisuudet ovatkin syy miksi polypropeeni edelleen kiinnostaa tutkijoita. Diplomityössä polypropeenin ominaisuuksia esitellään yleisellä tasolla. Yksi tämän diplomityön tärkeimmistä tavoitteista oli selvittää polypropeenin ominaisuuksia kestävän kehityksen kannalta. Näitä ominaisuuksia tarkastellaan työssä elinkaaritutkimuksen avulla. Elinkaaritutkimus, joka suoritettiin tätä työtä varten, vertaa polypropeenin ja eräiden matkapuhelimissa käytettyjen muovien energian kulutusta ja tuottamia kasvihuonekaasuja. Tässä työssä esitellään myös biopolypropeeni sekä käsitteenä, että mahdollisena tulevaisuuden materiaalina. Myös biojalostuksen periaate ja joitain sen mahdollisia raaka-aineita esitellään. Työssä tarkastellaan myös sekä polypropeenin nykyiset että tulevat markkinat ja teollisuuden kehityssuunnat. Diplomityössä käsitellään myös materiaalien käyttöä matkapuhelimissa sekä yleisesti että tarkemmin muovimateriaalien osalta. Muovimateriaaleissa keskitytään muoveihin, jotka voisivat olla mahdollisesti korvattavissa polypropeenimuoveilla. Tällä hetkellä polypropeenimuoveja käytetään matkapuhelimissa jonkin verran, muttei rakenteellisissa osissa kuten kuorissa. Toinen tärkein päämäärä diplomityölle onkin selvittää voitaisiinko polypropeenimuoveja käyttää matkapuhelimissa laajemmin kuin nykyisin. Tätä mahdollisuutta tutkitaan vertailemalla muovien ominaisuuksia kirjallisuudesta sekä käytännössä ruiskuvalutesteillä. Ruiskuvalutesteihin muovit valittiin mekaanisten ominaisuuksien perusteella käyttämällä vertailuarvoina joidenkin tällä hetkellä matkapuhelimissa käytössä olevia muovimateriaalien arvoja. Testaus suoritettiin kolmelle polypropeenimuoville ruiskuvalamalla muovit matkapuhelimen kuoren kaltaisiksi testikappaleiksi. Ruiskuvalutesteillä tutkitaan muovien valettavuutta sekä joitain muovin ominaisuuksia, kuten kutistumista. Ruiskuvalutestien tuloksista selviää, kuinka hyvin testatut polypropeenimuovit sopivat halutunlaisten osien tuottamiseen ruiskuvalulla. Nämä testit eivät kuitenkaan kerro sitä, soveltuvatko testikappaleiden mekaaniset ominaisuudet haluttuun käyttöön.

PREFACE

This Master Science Thesis was done for the Environmental Management team of Nokia Corporation. The team works in the field of environmental issues and environmental development. The thesis has been written between September 2010 and April 2011.

I would like to thank my supervisors M.Sc. (Technology) Ilona Santavaara and M.Sc. (Engineering) Mika Pelto. Their guidance and constructive criticism were valuable during this process. Special thanks for Ilona Santavaara for practical guidance and companionship in Nokia Corporation during this time. I would also like to thank Professor Minna Kellomäki for examining my thesis. I wish to express my gratitude to Matti Rahko, who was my supervisor in Nokia Corporation, for giving me the opportunity to do the thesis with such an interesting topic. I would also like to thank Shin Takayama and Kari Hiltunen from Nokia Corporation and Mikko Silvennoinen from Lite-On Mobile for their advices and assistance. The last but not the least I would like to thank my family and friends for supporting me during the thesis project and studies.

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ABBREVIATIONS, TERMS AND DEFINITIONS

ABS	Acrylonitrile-butadiene-styrene
ABS+PC	Acrylonitrile butadiene styrene and polycarbonate blend
CAMPUS	Computer Aided Material Preselection by Uniform Standards
GF	Glass fiber
GHG emissions	Greenhouse gas emissions
IPCC 2007 GWP 100a	Intergovernmental Panel on Climate Change 2007 Global Warming Potential 100 years
LCA	Life Cycle Assessment
MFI	Melt flow index
MFR	Melt flow rate
m.t.	Metric tonne
MWD	Molecular weight distribution
PA	Polyamide
PBT	Polybutylene terephthalate
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene terephthalate
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PPS	Poly(*p*-phenylene sulfide)
PS	Polystyrene
PVC	Polyvinyl chloride
T_g	Glass transition temperature
T_m	Melting temperature

Biopolymer	Polymers that can be found from nature, like starch cellulose or proteins.
Impact assessment method	LCA tool, which contains a quantity of complete impact categories.
CAS registry number	Chemical Abstract Service numbers are unique numbers to chemical substances, chemicals and compounds.
Clamping force	Clamping force is the force in which an injection molding machine may hold mold's halves together.
Engineering plastics	Plastics that are evolved further that mass production plastics usually are more expensive than them. Some engineering plastics: ABS, PC, PMMA, PA, PET
Holding pressure	The pressure that is maintained in injection cylinder after injection, try to compensate shrinkage of material in mold in cooling.

Mass production	Process methods, that can produce lot of products in at a short period of time, can be computer controlled and can be automated.
Mass production plastic	Plastics like PP and PE, that are quite inexpensive and they are utilized everyday products. Can be manufactured mass production methods.
Molecular mass	An alternative and more accurate term with polymers for molecular weight.
Molecular weight	The sum of the atomic weight of all atoms in a molecule.
Melting point	Same as the melting temperature
Melting temperature	The temperature where crystallization structure of polymer disappears. T_m
Plastic	Includes a polymer and additives, filler and/or reinforcements.
Polymer	A large molecule chain that consists of multiple small units.
Polyolefins	Structurally the simplest polymers: PP and PEs.
Switch over point	The point in injection molding when high pressure molding is switched to lower holding pressure.
Tacticity	Stereoisomerism of polymer that is determined in polymerization. Tacticity possibilities of polymer are: isotactic, atactic and syndiotactic.
Thermoplast, thermoplastic	Polymers that can be remolded with heat
Thermoset	Polymers that cannot be remolded with heat

1. INTRODUCTION

This study is Master of Science Thesis and it is done for Nokia Corporation (Nokia). Mostly the thesis is done as literature study. One reason to do the thesis is because about 45 % of a Nokia mobile device is plastic, including thermosets and thermoplastics [67]. Trend of plastic industry is changing to more ecological products and also consumers are starting to become more ecologically conscious. Against this background it is important to search for more eco-friendly and sustainable possibilities for plastics which are currently utilized in products of Nokia.

Polypropylene (PP) plastics were chosen as the subject for this study because their sustainability and mechanical properties needed to be studied. The most important goal of the thesis is to examine if PP plastics can be utilized in Nokia mobile phone covers. Currently PP plastics are used in small amounts in some of parts of Nokia mobile phones. Nokia has done a similar study earlier, but at that time PP plastics were not found suitable for the wanted use. However, research and development in the plastic industry are continuous and rapid, and thus the previous results are already outdated. Another goal for the thesis is to survey current PP materials on the market and their suitability to requirements set by Nokia.

One of the goals is also to show sustainability of polypropylene versus other plastics. This is done with Life Cycle Assessment (LCA). LCA study is currently an important tool when comparing environmental impact of the life cycle of a material or a product. An LCA study that is performed for this thesis, compares some of the plastics which are commonly used in mobile phones.

Other goals of the thesis were to study if properties of reinforced PP are appropriate for utilizing it in products and whether polymerization method has an impact to properties of PP plastics. Furthermore, biopolypropylene usage was also surveyed. Biopolypropylene is a plastic which is manufactured from renewable sources or conventional PP plastics which contain some renewable material like starch. Market situation was also investigated, to find new conventional and bio-based PP materials. Bioplastics and their development are a part of the plastic industry that changes rapidly. Present studies in the field of bioplastics are an evident indicator of this development and properties of bioplastics are developing closer to industrial plastics.

Polypropylene forms with polyethylene (PE) the group of polyolefins, which are structurally the simplest polymers. Polypropylene is also a thermoplast, so it can be remolded with heat, whereas thermoset plastics cannot be remolded. Furthermore, polypropylene is one of the mass production plastics alongside PE, polystyrene (PS) and polyvinylchloride (PVC). In some European statistics polyethylene terephthalate (PET)

is also categorized as a mass production plastic. [25] Mass production plastics are quite inexpensive and they are utilized in everyday products. These plastic products are usually manufactured quickly with automated manufacturing methods like injection molding. Usually the mechanical properties of mass production plastics are rather poor when compared to the properties of engineering plastics. Engineering plastics, like polycarbonate (PC), polyamides (PA), poly(methyl methacrylate (PMMA) and acrylonitrile-butadiene-styrene (ABS), are more expensive and they are utilized when a specific property is required. Furthermore, engineering plastics can be used in many cases as replacements for metals or glass, especially when high strength-to-weight ratio is needed [10]. However, mass production plastics may be developed further so their properties would be closer to properties of engineering plastics [25]. Properties of polypropylene that are presented within this thesis are general values, because polypropylenes and additives form a group of versatile PP plastics. Properties are also not related to any specific PP plastic grade. Because of the final goal of this thesis, the investigated properties focused mainly on injection moldable PP plastics.

This thesis is divided into nine chapters. The second chapter of the thesis *Polypropylene* introduces polypropylene in general, properties of polypropylene and processing methods. Some different polypropylene plastics are also presented. The third chapter *Sustainable advantages of polypropylene compared to other plastics* concentrates on LCA and LCA studies. In this chapter, some plastic LCA studies are presented, as well as results of an LCA study which was performed for this thesis. The study concentrates on plastics which are currently used in mobile phones. In the fourth chapter *Review of biopolypropylene and biorefinery concepts* biopolypropylene and biorefinery concepts are introduced. In the fifth chapter *Market survey and industry trends* prices of polypropylene and some other commonly used plastics are considered as well as markets and current and coming industry trends of polypropylene. The sixth chapter *Plastics in mobile phone applications of Nokia* concentrates on materials that are utilized at the moment in mobile devices of Nokia and their properties in comparison to properties of polypropylene. The comparison is done using the values which are found in literature. The seventh chapter *Testing of the selected PP plastics* discusses how PP plastics were chosen for testing and what kind of different tests were done to ensure injection moldability of chosen PP plastics. Test results are also presented and discussed. The eighth chapter *Conclusion* summarizes the thesis including the literature study and the injection moldability tests. The last chapter *Suggestions for future studies* includes some recommendations for future studies and some issues to be followed up are mentioned.

2. POLYPROPYLENE

This chapter introduces polypropylene as a polymer, properties, processing, and some health concerns related to it. Furthermore, the chapter also provides some information of polypropylenes nomenclature and other general issues. Also the distinction between polymer and plastic is explained.

2.1. General information about polypropylene

Polypropylene was invented in the 1950's. In the past 30 years development of this thermoplastic polymer has been significant. Development of polypropylene has turned it to the second most used plastic much due to its versatile properties. Polypropylene is used in different applications and shapes and it can be processed with various techniques such as injection molding, extrusion and thermoforming into a variety of products: fibers, films, pipes, injection molded packages, sheets and car parts. During the year 2007, 9200 million kilograms of polypropylene were used in Europe. [25]

Polypropylene CAS (Chemical Abstract Service) Registry number is 9003-07-0 [18]. Each unique chemical structure has a unique CAS Registry number. The unique number helps identification of chemicals so that the identification is possible and becomes easier even if the name is not common. The number itself does not have chemical significance. [49]

Nomenclature of polypropylene is relatively simple. The name of polypropylene is formed by attaching a prefix *poly* "many" in the front of monomer's *propylene* name. [10] Propylene is an older, more common name for propene which is the name of the chemical structure according to nomenclature rules of IUPAC (International Union of Pure and Applied Chemistry) [12]. So according to nomenclature rules of IUPAC the name is polypropene. However, the name polypropylene is still commonly used in polymer industry and therefore it is used also in this thesis.

Polypropylene is a polymer chain which consists of mer units [6]. The mer unit is explained in detail in Section 2.2. The structure and molecular weight of the mer unit of the polypropylene are always the same. However, polymer chains are not identical as their properties like spatial arrangement, tacticity (explained in Subsection 2.3.1.), and molecular weight may differ [6]. Molecular weight of a polypropylene chain is comparable to the length of the chain. PP plastics consist of multiple polypropylene chains. Furthermore, PP plastic usually contains some additives in addition to polypropylene polymer [6]. There are a number of factors, like polymerization method, additives, fillers and reinforcements, which affect the properties of polymer and PP plastics. Polypropylene is not a single plastic with certain properties, but a group of

plastics that have different properties [4]. So when speaking of properties of polypropylene they are generalizations, which give a general view of this versatile plastic. When searching for a material for a specific application, all properties need to be observed and confirmed.

2.2. Polymerization

Polypropylenes are manufactured of propene monomers which are typically obtained from oil-refinery as gaseous byproducts [32]. The propene monomer is illustrated in Figure 2.1. Polymers are manufactured of monomers by polymerization. In the polymerization the monomers are attached together to form a polymer chain. When two propene monomers are attached together in polymerization, a double bond of propene breaks so that carbon can attach to first or second carbon of another propene. This continues and each new monomer is attached to a form a polymer chain. Figure 2.2. shows a part of a polypropylene chain after polymerization. Generally polypropylene is manufactured by chain-growth polymerization [10]. There are different polymerizing methods for manufacturing polypropylene and some of the methods are explained in Subsections 2.2.1 and 2.2.2. [32]

Polypropylene is manufactured from propylene monomers. However, it can be said that polypropylene polymer consists of a repetitive mer unit, as the name *poly*mer suggests. Structure of the mer unit is different from structure of the monomer. [6] Figure 2.3. illustrates the mer unit of polypropylene.

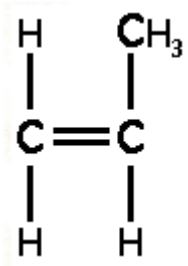


Figure 2.1. *Monomer of polypropylene; propene.*

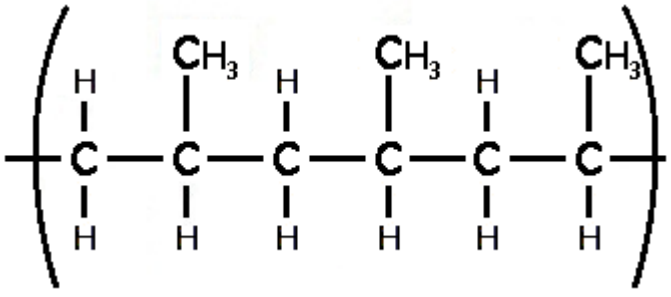


Figure 2.2. *Part of a polypropylene chain. Chain continues alike in both directions.*

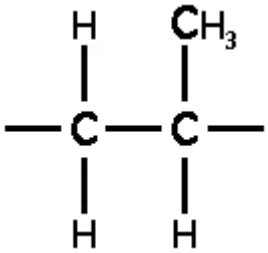


Figure 2.3. *Mer unit of polypropylene.*

Catalysts are used in the polymerization of polypropylene. Catalysts are substances which start or accelerate the polymerization reaction, but they are not consumed in the reaction. By using catalysts it is possible to increase the yield of a polymer in polymerization. Polymerization catalysts are usually organometallic transition metallic complex compounds. They attach to a growing polymer chain and hold it at close proximity to monomers so they can react. The catalysts also provide active sites where the polymerization can occur. The catalysts of polypropylene were developed and taken into use in the 1950's. The catalysts enabled the production of stereospecific polymers which are utilized to this day. Stereospecificity means attachment of propene molecules to form a polypropylene chain in a particular orientation so it lengthens the forming chain. [32]

2.2.1. Ziegler-Natta catalyst polymerization method

One utilized polymerization method is Ziegler-Natta polymerization. Ziegler-Natta polymerization is a subtype of chain-growth polymerization. This method uses Ziegler-Natta catalysts which are from the periodic table groups I-III bimetallic coordination complex of a metal cation and from the groups IV-VIII transition metal compound. [10]

Ziegler-Natta polymerization forms a polymer which is up to 98 % isotactic. Tacticity is explained in detail in Subsection 2.3.1. [10] Ziegler-Natta polymerized polypropylenes contain polypropylene molecules which have a wide range of molecular weights and some branching. For a thin wall injection molding or film applications, the Ziegler-Natta manufactured polypropylene needs to break down chemically or thermally because of the size of the molecule. After breaking down the polymer is easier to process. [32]

2.2.2. Metallocene catalyst polymerization method

In metallocene polymerization metallocenes are used as the catalyst. Metallocene polymerization is also a subtype of chain-growth polymerization. [10] Usually metallocenes from the periodic table group IV they are organometallic compounds which have transition metals like zirconium, titanium or hafnium in between two cyclic organic compounds. The spatial structure of metallocenes resembles that of a sandwich. [32] The basic structure of a metallocene is illustrated in Figure 2.4. Normally metallocene catalysts are used with a co-catalyst. Generally the most used co-catalyst is

methylaluminoxane (MAO). [10] The co-catalyst substantially increases polymerization rate. [32]

Ansa-metallocene catalysts have a bridge between two indenyl ligands. In the 1980's it was discovered that the ansa-metallocenes produce isotactic polypropylene. Ansa-metallocene polymerization process is easy to alter by changing indenyl ligands of the catalyst. This affects the melting temperature (T_m) and the molecular weight of the forming polymer. Depending on the ligand, T_m of the forming polymer can vary between 137-162 °C and molecular weights can vary between 36 000-990 000 g/mol, respectively. [31]

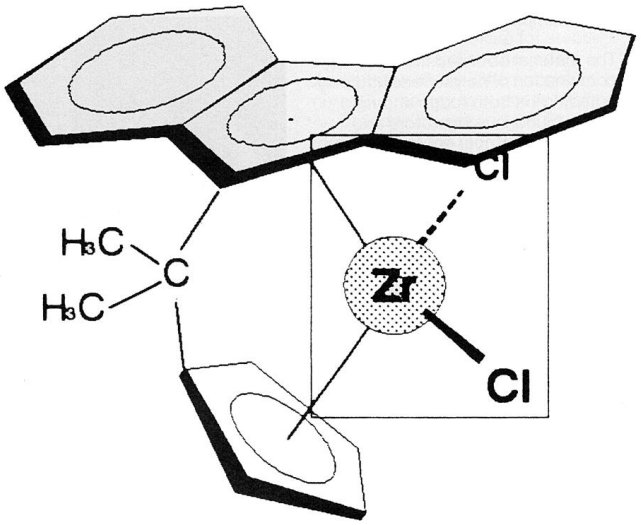


Figure 2.4. *Sandwich-like spatial structure of a metallocene catalyst. [32]*

Metallocene polymerized polypropylenes have high rigidity, transparency, heat distortion temperature, impact strength and toughness. They have also low extractables level. Catalyst residues may cause yellowing when they react with additives. [32] Metallocene catalyst polymerization method can be altered so that the tacticity of the polymer can be varied over a wide range. Due to this it is possible to tailor the synthesis and produce the needed polypropylene. [2] With metallocene polymerization it is possible to obtain uniform polymers which have narrower molecular weight distribution (MWD). Metallocene polymerization process is more expensive than Ziegler-Natta polymerization, but on the other hand metallocene catalyst is more effective and produces more polymers per quantity of the catalyst. [10]

2.3. Properties

2.3.1. Tacticity

Tacticity is stereoisomerism of polymer and it is determined in the polymerization [6]. Polypropylene can be isotactic, syndiotactic or atactic. The used catalyst has an effect on how different tacticities are arranged in a polypropylene chain. Usually

polypropylenes are predominantly isotactic which have short atactic sections. Tacticity of polymers affects its crystallinity which has an effect on mechanical properties such as stiffness and tensile strength. [32] Isotactic and syndiotactic polypropylenes are crystalline [10]. Isotactic polypropylene has the highest crystallinity, which leads to good mechanical properties such as stiffness and tensile strength. Syndiotactic PP has lower crystallinity and it is not as stiff as isotactic polypropylene, but syndiotactic PP has better impact strength and clarity. [32]

Atactic polypropylene is an amorphous material, which is a result from its irregular chemical structure [32]. Chemical structures of isotactic and syndiotactic polypropylenes are regular. In the isotactic polypropylene all methyl (CH_3) groups are on the same sides of the polymer chain whereas in the syndiotactic polypropylene methyl groups are altering on both sides of the chain alternately. In atactic polypropylene methyl groups are at both sides of the polymer chain irregularly. [10] Tacticity possibilities of polypropylene chains are illustrated in Figure 2.5.

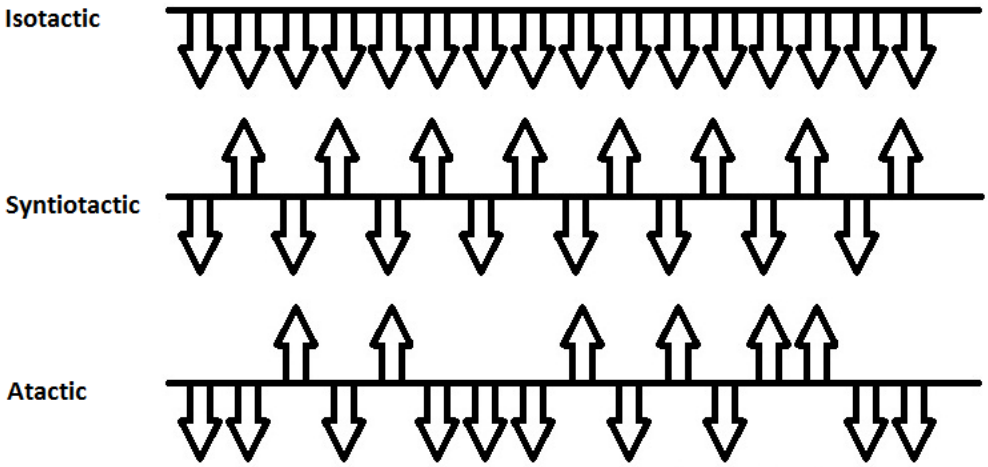


Figure 2.5. *Tacticity possibilities. Arrow points in the direction of the CH_3 group. Modified from [10]*

By changing polymerization conditions, especially temperature and monomer concentration, it is possible to control to some extent the tacticity of polymer. In this way it is possible to affect the relative amount and average length of isotactic and atactic sequences in a polymer chain. [4] Amount of atactic sequences in an isotactic polymer chain affects the properties of polypropylene. [32] Table 2.1. illustrates how properties of the polypropylene change when the amount of atactic sequences increase.

Table 2.1. *Increased atacticity affects some of the properties of polypropylene. Modified from [32]*

Property	Increasing Atacticity
Impact Resistance (room temperature)	↑
Elongation	↑
Shear Rheology	↑
Heat Seal Strength	↑
Irradiation Tolerance	↑
Extractables (solubility)	↑
General Optical Properties	↑
Haze in Films	↓
Crystallization Temperature	↓
Stiffness	↓
Long Term Heat Aging Resistance	↓
Color Quality	↓
Melting Temperature	↓
Heat Distortion Temperature	↓
Moduli	↓
Strength	↓

2.3.2. Crystallinity

Polypropylene is a semi-crystalline material. Therefore, in polypropylene there are crystalline and amorphous regions. [6] Crystallization starts when the temperature of polymer melt is cooled below the T_m. When the temperature is decreasing a crystalline polymer begins to solidify, in other words to crystallize. Crystals are organized units, they may be formed spontaneously or they may be induced by a foreign particle, for example, nucleating agents that are explained in Subsection 2.5.1. The crystallization rate is dependent on the nucleation rate and the rate of crystal growth. The optimal crystallization temperature is usually about 80 percent of T_m, which is when the crystallization rate is at its greatest. Usually in slow cooling degree of crystallization is higher. Degree of crystallization may be controlled with quenching, subsequent annealing or suppressing crystallization by rapid cooling. [32] Crystallization degree of polymer during the melt process depends on polymerization rate and how long the melt temperature is maintained [10]. If the crystallization occurs rapidly, like in injection molding, polymer chains can be crystallized to more than one lamella. [32]

When polymer crystallization starts, polypropylene chains begin to form helical structures. Methyl side groups of polypropylene affect the shape of helical structures. Because of bulkiness of a methyl group, chains cannot pack closely and the shapes of the helical structures are distorted. The helical polymer chains form plate-like or ribbon-like structures, lamellae, by folding; typical lamellae are 2-50 nm thick. Thickness depends on crystallization temperature and processing methods. Lamellae which grow radially form spherulites, which are 1-50 μm wide spherical structures that have a

central point. The shape of a spherulite is illustrated in Figure 2.6. Size of spherulite affects the strength and ductility of polypropylene. Spherulites formed in higher crystallization temperature have are bigger, which results in more brittle behavior. When the cooling rate increases spherulite size decreases and the forming material becomes more ductile. Spherulite size and clarity are tangled, so that smaller spherulite size enhance clarity. [32]

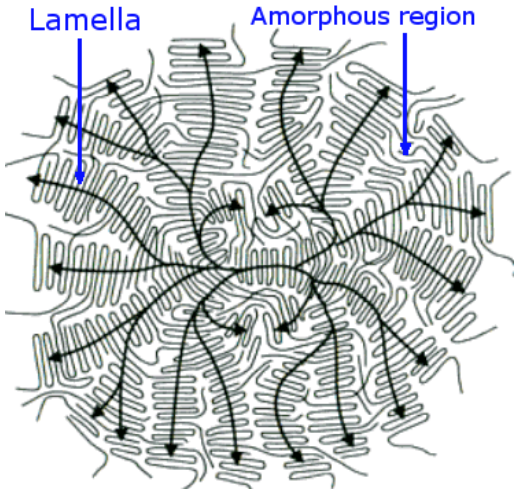


Figure 2.6*. Spherical shape of a spherulite, folded lamellae and amorphous regions between lamellae. [17]*

2.3.3. Molecular weight of polypropylene

Physical behavior of polypropylene is a result of combination of the microstructure of the chain, the average molecular weight and the MWD [4]. The molecular weight and MWD affect properties and processing possibilities of polypropylene. If molecular weight is high the polymer chain is long. The average molecular weight for polypropylenes in general is within a range of 220 000-700 000 g/mol. From the average molecular weight it is possible to estimate melt flow index (MFI) because MFI and the average molecular weight have an inverse relationship. Variations in molecular weight have a direct effect on the toughness of polypropylene: higher molecular weight means higher toughness. Increasing molecular weight improves some properties of polypropylene and decreases others. [32] Table 2.2 presents how increasing molecular weight affects some of the properties of polypropylene.

Polypropylenes consist of a multitude amount of polymer chains with various lengths and molecular weights. MWD shows variations of molecular weight in certain polymer grade. Narrow MWD means that most the polymer chains are approximately same length. Broader MWD means greater chain length variation. MWD affects the processing ability of polypropylene, as polypropylene with broad MWD is more sensitive to shear than narrower MWD polypropylene. [32]

Table 2.2. *Increasing molecular weight affects some of the properties of the polypropylene. Modified from [32]*

Property	Increasing Molecular Weight
Die Swell	↑
Melting Temperature	↑
Impact Resistance	↑
Elongation	↑
Shear Rheology	↑
Heat Seal Strength	↑
Irradiation Tolerance	↓
Extractables (solubility)	↓
Haze	↓
Crystallization Temperature	↓
Heat Distortion Temperature	↓
Moduli	↓
Strength	↓

2.3.4. Melting- and glass transition temperatures

Melting point or melting temperature (T_m) of the polymer is the temperature when the crystalline structure of solid polymer disappears [32]. In the T_m the net crystallization rate is zero since crystalline lamellae are dispersed as fast as lamellae are formed from the polymer-melt [10]. In the T_m physical properties of the material change as material becomes a viscous liquid. Crystallinity affects T_m of polypropylene. [32] For high crystalline polypropylene the T_m can be up to 200 °C [10]. T_m of isotactic polypropylene varies from 160 °C to 171 °C. Lower crystallinity lowers the T_m, for example T_m of syndiotactic polypropylene is approximately 130 °C. [32] The melting of polymer occurs over a range of temperatures, because polymer materials are comprised of molecules which have a variety of molecular weights. As a result a polymer has a range of T_m's rather than a single melting temperature. [6]

In glass transition temperature (T_g) amorphous regions of the polymer transform from liquid or rubbery state to a solid and rigid state [6]. In the T_g the crystallization rate of polymer is zero [10]. T_g of polypropylene can vary from -35 °C to 26 °C depending on heating rate, thermal history and microstructure of the polymer. Measurement method also has an effect on the T_g [32].

Normally polymers are utilized and processed between the T_m and the T_g, when the strength and stiffness of the crystalline region are combined with the toughness of the amorphous regions [32]. Also the crystallization rate is the highest between the T_m and the T_g [10]. When selecting fabrication or processing procedures of the polymer, T_m and T_g of the polymer need to be observed. [6].

2.3.5. Chemical resistance

As a non-polar molecule polypropylene is chemically weak against non-polar molecules albeit it is chemically more resistant to polar solvents like soaps. It also has good chemical resistance to other polar molecules such as alcohols, organic acids, esters and ketones. It is also resistant to most inorganic acids and alkalis. [32]

Polypropylene is chemically weak against strong oxidizing acid halogens. Non-polar solvents like liquid hydrocarbons or chlorinated solvents may cause swelling, softening or surface grazing. Fuming nitric acid and hot, concentrated sulfuric acid may as well cause swelling and degradation. Copper and copper alloys accelerate oxidations especially in reinforced polypropylenes. Crystalline polypropylenes are more chemically resistant than amorphous polypropylenes [32].

2.4. Copolymers and blends

There are PP homopolymers and PP copolymers. PP homopolymer contains only propene monomers, copolymers on the other hand contain at least two different types of monomers. In PP copolymer other monomer is usually ethylene. Homopolymer and copolymers have different mechanical and chemical properties. Copolymers are produced by adding comonomers to the reactor during polypropylene polymerization. [32]

There are different types of copolypropylenes: block, random, alternating and graft copolymers [10]. Different copolymer possibilities are illustrated in Figure 2.7. Block- and random copolymers are the most common types. In the random copolymer comonomers randomly take place of the propylene in the forming polymer chain. In the block copolymer comonomers are in blocks in the polymer chain. [25]

Generally random copolymer contains 1-7 wt% of ethylene. Spatial structure of random copolymer is similar to the structure of an isotactic polymer. Random copolymers are typically used in film, blow molding or injection molding applications which require clarity, good impact strength at low temperatures, stiffness and a moisture barrier. [32]

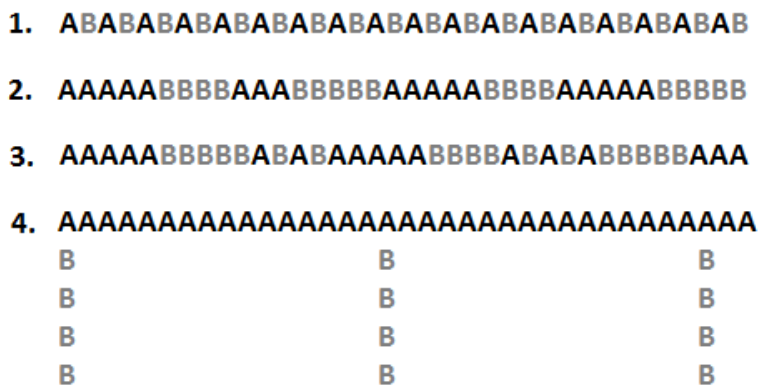


Figure 2.7*. 1. Alternating copolymer 2. Block copolymer 3. Random copolymer 4. Graft copolymer. Copolymers consist of two types of monomers, which A and B stand for. Modified from [10]*

One good example of a well-known copolymer is ABS, which monomers are acrylonitrile, butadiene and styrene [10]. ABS is used in many applications such as garden equipment and toys like Lego bricks and in mobile phones where it is blended with PC [6, 25].

PP plastics are also blended with other plastics. When polymers are blended, properties of the blend are a combination of both components properties. Furthermore, some of the blends properties, such as T_g, may be intermediate of the components properties, but all of the properties do not behave likewise. [10]

2.5. Additives

Various foreign substances, additives, are added to polypropylene resins to improve material properties. The additives are added during processing or applied to the surface of a finished part. [32] With the additives it is possible to alter mechanical, chemical or physical properties more than merely altering of the fundamental molecular structure of the plastics would achieve [6].

2.5.1. Nucleating agents and stabilizers

Nucleating agents increase the number of initiation sites for the crystallization. Subsequently forming spherulites are smaller and more numerous. This has effects on mechanical properties, processing characteristics and clarity of polypropylene. Nucleating agents which are used in polypropylene are carboxylic acid salts, benzyl sorbitols and organic phosphate salts. Also some pigments, like phthalyl blue, can act as nucleating agents. Nucleation alters mechanical properties like tensile strength, stiffness, flexural modulus, impact strength and heat deflection temperatures. [32]

Degradation of polypropylene is especially caused by ultraviolet light (UV) or oxidation. Stabilizers are additives which counteract these threats of the polypropylene. [6] Oxidative degradation of polypropylene occurs particularly at elevated temperatures. The oxidative degradation decreases molecular weight and properties that are dependent

on it. To prevent this behavior antioxidants are added to polypropylene, usually this is done immediately after the polymerization. Antioxidants that are used in polypropylene are hindered phenolics, like butylated hydroxyltoluene (BHT). [32]

Photo degradation of polypropylene is caused by UV light at wavelengths of 290-400 nm. UV light causes free radical forming, which in turn causes chain scission and decrease of mechanical properties. UV absorbers (UVAs) are optical filters that absorb UV light and release the excess energy as heat. They are photo-stable molecules which have high absorption in wavelengths of 290-400 nm. UVAs that are used in polypropylenes are benzophenone derivatives, benzotriazoles, aryl esters and formamidines. UVAs have an effect on properties of polypropylene such as solubility, volatility and compatibility of resin. [32]

2.5.2. Catalyst deactivators and colorants

When polymer is manufactured, some of the used polymerization catalyst may be left in the final product. These catalyst residues may cause yellowness in the product if they react with additives. Catalyst deactivators are added to neutralize catalyst residues and to prevent unwanted color change of the product. [32]

Pure polypropylene is a white nearly transparent material that may be colored with various coloring methods such as dyes or pigments [32]. Molecules of a dye dissolve and become a part of the chemical structure of the polymer [6]. However, they are not compatible with all polypropylene grades [32]. Pigments, on the other hand, remain in a separate phase in the polymer [6]. Pigments are available in various types from dry powders to liquids and they can be organic or inorganic compounds. They are more compatible with polypropylene grades. The quality and outcome of coloring depends on how well the colorant is dispersed to the polymer melt. Coloring method can have an effect on manufacturing costs of polypropylene. [32]

2.5.3. Flame retardants and antistatic agents

Flame retardants reduce ignitability and combustion rate. They can be reactive or additive. In thermoplastics like polypropylene flame retardants which are primarily used are additives. These are mixed during polymerization or immediately after it. [32] The flame retardants have multiple ways of working, such as interfering combustion process or initiating a chemical reaction which causes cooling and cessation of burning [6].

Polypropylene is an insulator. However, the surface of a PP product can build up with static charge, which can accumulate dust to the surface of a product. Antistatic agents (antistats) can be ionic or nonionic, internal or external. Nonionic antistats are commonly used in polyolefins. For example, glycerol monosterate is used in injection molded polypropylene. Internal antistats are compounded with the polymer, they continually migrate to the surface of the polymer forming a thin layer which does not alter the appearance of the polymer part. External antistats are applied to the surface of products after the manufacturing. [32]

2.6. Fillers and reinforcements

Properties of the polymers can be altered with fillers and reinforcements. However, fillers and reinforcements always affect the mechanical properties of the plastic, whether wanted or not.

2.6.1. Fillers

Fillers are materials which are added into polymer during the manufacturing process. Fillers are used to decrease the amount of polymer needed and hence reduce costs or additionally alter wanted mechanical properties of polymer. Fillers also change properties of polypropylene resin, which also leads to changes in casting and molding properties of the polymer. Fillers that are used as extender material are usually inexpensive materials such as calcium carbonate or talc, which may improve stiffness of the polymer. Filler materials that are used as reinforcements are mica, wollastonite and glass, they are usually fiber-shaped. [32]

Some organic materials, like wood flour or flax, can be utilized as fillers as well. When filler materials are organic, processing temperatures of the polymer need to be altered. [32]

2.6.2. Reinforcements and composites

Composite is typically defined a combination material which consists of two or more elements: matrix and reinforcements. The matrix is the body which defines the dimensions of the composite. Reinforcements which often are fibers, are load-bearing. Composites can consist of several materials or only one material, for example PP fibers in PP matrix. Composites are often created to improve mechanical properties of pure materials. [6]

Glass fibers (GF) are used as reinforcement in polypropylene composites. The fibers improve stiffness and fracture toughness. Long glass fibers provide better improvement compared to shorter glass fibers. For example, Hartikainen *et al.* studied polypropylene hybrid composites with long glass fiber and talc filler. They found that despite the filler decreasing costs of the material and improving its modulus, other mechanical properties decrease. [13]

In addition to conventional reinforcements in polymer such as glass or carbon fibers, natural fibers can be used as well. Natural fibers can be divided into three groups: bast, leaf and seed or fruit fibers. Bast fibers can be obtained from bananas, jute, flax, hemp and kenaf. Leaf fibers are obtained from plants, like pineapple, sisal or screw pine. Seed or fruit fibers can be obtained from cotton, oil palm and coconut. [33] These fibers have some advantages compared to glass or carbon, for example cost, lower density, biodegradability, high specific properties and being non-abrasive during processing [14, 33].

When manufacturing polypropylene composite with natural fibers the hydrophobic polymer matrix and the hydrophilic fibers may cause weak adhesion and poor fiber dispersion [28]. A coupling agent can improve the matrix and fiber adhesion. One of the used coupling agents in PP composites with natural fibers is maleated polypropylene (MAPP) [27]. There are various MAPPs which can be used as coupling agents. For example, with one coupling agent, some mechanical properties of a composite may be improved almost by 60 % with 3 % share of the coupling agent. [28]

Reinforced polypropylenes and composites are available on the market, some of these are introduced in Section 2.9. Natural fibers from wood and oil palm's empty fruit bunch as well as cellulose from oil palm are studied as reinforcements in the PP matrix composites [27, 29]. Khalid *et al.* discovered that cellulosic fibers can improve mechanical properties of polypropylene. The mechanical properties may improve further by using suitable coupling agent like MAPP. [29] The cellulosic fibers improve stiffness and strength of the composite but decrease its toughness [14].

2.7. Processing

The most widely used processing methods of polypropylene, injection molding and extrusion, are both melt processes. Injection molding will be discussed in further detail in next Subsection. Other processing methods that are used with polypropylene are blow molding, thermoforming and calendering. There are also several decorating methods like painting, metallization, printing and application of surface coverings. With these methods it is possible to work with the surface of a PP product. Properties of polypropylene, like MWD and MFI, affect how molten polypropylene behaves and which polymer grades are suitable for which processing methods. Polypropylenes with broader MWD are used in injection molding, whereas narrower MWD polypropylenes are used in extrusion. [32] MWD of polymer has an effect on MFI and it may be used to characterize the structure of polymer.

2.7.1. Injection molding

As mentioned before, injection molding is one of the most used processing methods for products made of PP plastics. Injection molding is explained in more detail than other processing methods because some parts of mobile phones are manufactured utilizing it. Furthermore, it is also used when materials are tested, more about testing in Chapter 7. An injection molding machine that is illustrated in Figure 2.8. consists of several units. Some of these units are: a plastication unit, a clamping unit, a control unit, and temperature control. The plastication unit plastifies, meters, stores, and injects the molten plastic. The clamping unit contains the mold and moves the other half of the mold. However, the mold itself is a separate unit. Furthermore, the clamping unit contains also an ejection mechanism for the product. [3] Molds of injection molding machines are replaceable. Temperature of the mold is controlled with the temperature unit [3]. Injection molding machines are classified according to their clamping force,

which can be from 125 kN up to 55 000 kN. Clamping force is the force with which an injection molding machine may hold halves of the mold together. [22]

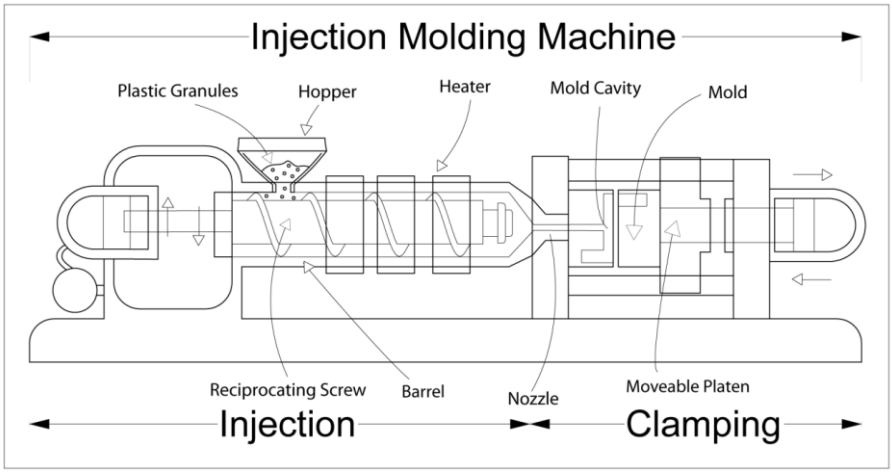


Figure 2.8. *Injection molding machine [34].*

Injection molding cycle time is the time taken for manufacturing one product and usually it is something from 10 to 30 seconds [6]. However, cycle time for a simple thin-walled product can be a mere 1 second and cycle time for a bulky thick-walled product can be several minutes. Injection molding cycle time consist of seven sections: closing the mold, injection, holding pressure stage, cooling stage, metering, opening the mold and ejection. [3] Injection cycle is illustrated in Figure 2.9.

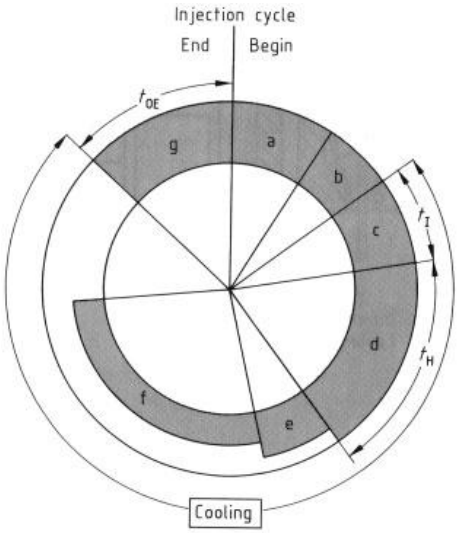


Figure 2.9. *Injection molding cycle time consist of seven sections. Usually cycle time is 10-30 s. a) Closing the mold; b) Moving the plasticating unit forward; c) Injection; d) Holding pressure phase; e) Moving the plasticating unit backward; f) Metering; g) Opening the mold and ejection of molding [3]*

The principle of injection molding is quite simple: plastic is melted and injected into the mold. Plastic granulates are loaded to hopper and usually granulates are dried before inserting as moisture could form bubbles in the plastic melt. From the hopper

granulates get into machine usually without external help. Inside the machine is a screw that moves first granulates and later molten plastic forward. The heater warms granulates while the screw moves them forward, while friction helps to melt the granulates. Molten granulates form a viscous liquid. The plastic melt is impelled through a nozzle to a mold cavity. Pressure is maintained while the molding solidifies. After it has solidified the mold opens and the molding is ejected. Once the mold has closed again, the cycle starts again. [5] As can be seen from Figure 2.9. polymer melt starts to cool when it is injected to the mold and the cooling continues until the product is ejected from the mold. Furthermore, while a product is in the mold, the injection apparatus is prepared to inject the next product. [3]

2.7.2. Processing parameters

In the melt process flow rheology of the polymer has an effect on processing. Rheology of polypropylene is dependent on temperature of polymer melt and shear rate. Processing parameters of polypropylene have an effect on each other. For example, injection molding parameters melt flow rate (MFR), injection pressure and melt temperature need to be adjusted together. When MFR is 4-10 g / 10 min, injection pressure is 500-1000 bar and temperature is 220-250 °C. If MFR is changed to be higher than 20 g / 10 min, injection pressure is then 400-1000 bar and temperature 200-230 °C. MWD of polypropylene has an effect on melt viscosity and thus also the shear rate. PP grades with broad MWD are more sensitive to shear than PP grades with narrow MWD. [32]

Thermoplastics are usually processed in when molten. When processing thermoplastics, the polymer is first melted and after molding the polymer needs to be cooled down. Polypropylene requires a vast amount of heat to melt. Comparing melt temperatures of polypropylene and polycarbonate and the energy they require to melt it is easier to see how demanding polypropylene is. Melt temperature of polycarbonate is 300 °C and for polypropylene it is 260 °C and the energy which they require to melt are 490 J/g and 670 J/g, respectively. Melt temperature of polypropylene is lower than that of polycarbonate but polypropylene requires almost 200 J/g more energy to melt than polycarbonate. Cooling of polypropylene is also more demanding. Polypropylene's and polycarbonate's heat removed in cooling and their mold temperatures are shown in Table 2.3. [32]

Table 2.3. *Differences between polypropylene and polycarbonate melt processing properties. Modified from [32]*

	Melt temperature	Mold temperature	Heat required to melt	Heat removed on cooling
PP	260 °C	20 °C	670 J/g	670 J/g
PC	300 °C	90 °C	490 J/g	368 J/g

2.7.3. Shrinking and warping

As polypropylene cools off it shrinks. Polypropylene is a semi-crystalline plastic and its crystalline regions shrink more than its amorphous regions which cause variations to shrinkage rates of the polypropylene. Shrinkage rate of polypropylene is related to the crystallinity degree of the plastic. Cooling rate has also an effect on the shrinkage of material. Overall shrinkage takes place in a period of time. For example, in an injection molded product most of the shrinkage is evident after removing the mold, but the product continues to shrink for more than 24 hours. This is caused by internal crystallinity and relaxation changes of polypropylene, which will cause small dimensional changes in the product. Shrinkage of polypropylene is difficult to estimate in advance, but the shrinkage can be minimized by using high viscosity, controlled rheology or non-nucleated grades. [32]

Fillers and reinforcements have an effect on shrinkage: fillers like talc or glass beads are likely to reduce shrinking. Reinforcement fibers reduce shrinkage as well. Because of their orientation during flow the reduction is greater in direction of the flow. Additives like nucleating agents can also affect shrinking. Mold nucleated polypropylenes shrink more rapidly than non-nucleated. [32]

Uneven shrinking causes warping and the product becomes distorted. Warpage can be minimized by using grades with narrow MWD and controlled rheology. Furthermore, fillers, like talc or glass beads, and additives have an effect on shrinking and warping. [32]

Figures 2.10. and 2.11. illustrate distortion of a plastic product caused by uneven shrinkage. The pictures have been made with Autodesk Moldflow Insight AMI2010 R2. Distortions in reality are small, however, in the figures the distortion is multiplied by 30 to make the distortion visible. Colors in the figures illustrate which direction the distortion occurs, blue and light blue are downwards and red, yellow and green are upwards. There is no clear zero level, but it is located between light blue and green. There are two plastic materials in the figures: PA-GF on the right hand side and PC+ABS on the left hand side. Like polypropylene, PA-GF is also a semi-crystalline material whereas PC+ABS is an amorphous material. As can be seen from Figures 2.10. and 2.11. different materials are warping differently. [41]

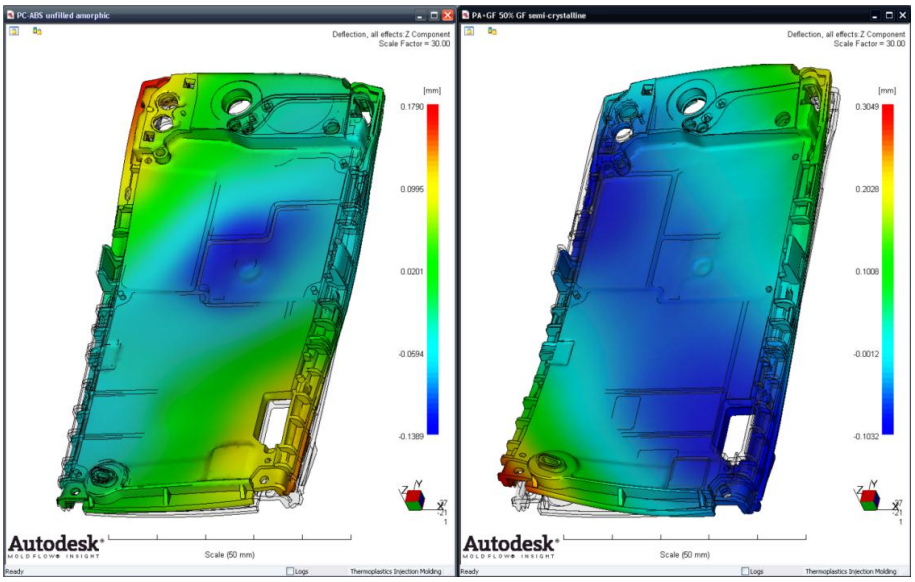


Figure 2.10. *Distortions of injection molded plastic product. On the left hand is PC+ABS and on the right hand side is PA-GF. [41]*

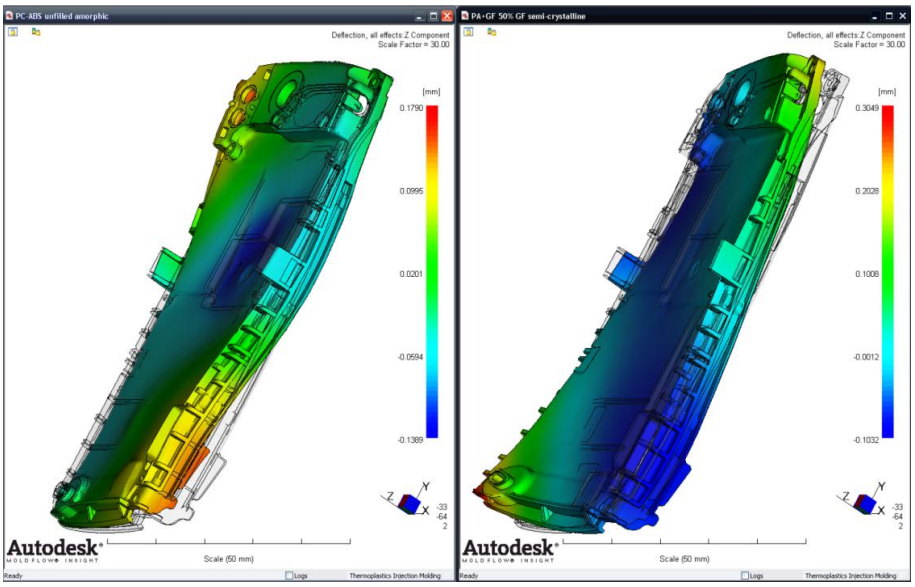


Figure 2.11. *Distortion of injection molded plastic products. On the left hand is PC+ABS and on the right hand side is PA-GF. [41]*

2.8. Variety of polypropylene forms

Polypropylene can be produced into different forms. In this chapter some of these forms and their manufacturing methods are introduced.

2.8.1. Fibers

PP fibers are used in carpeting, ropes or twines, textiles, automobile interior and nonwoven products like diapers. They are relatively easy to produce due to polypropylenes melt flow properties. [32] Fibers are produced by melt spinning.

Crystallinity of spun fibers depends on cooling rate during spinning. Furthermore, strength of fibers can be improved after forming by drawing. [6]

To PP homopolymer, fibers are one of the most important applications. Different kinds of fibers may be produced from polypropylene: monofilaments, multifilaments, fiber staple, slit tape, spunbonded fibers and melt-blown fibers. [32]

2.8.2. Films and sheets

A plate-like product whose thickness is less than 0.254 mm is considered as a film, anything thicker than this is considered as a sheet. [32] Thin films are 0.025-0.125 mm thick [6]. PP films are one of the most versatile packaging materials and they can be manufactured with various methods like casting and blow molding. The utilized method is dependent on desired properties of the film. [32]

PP films are used in packaging of food, stationery items, cigarettes, textiles, consumable and medical packaging, stickers, labels and personal hygiene products. Construction films can be made from polypropylene as well. Furthermore, PP film can be a component in multilayer films [5]. Multilayer films can be produced by coextrusion, where multiple polymer types are extruded simultaneously [6].

Sheets are thicker than 0.254 mm. PP sheets are manufactured, for example, by extruding. Sheets are formed to the desired shape with thermoforming. PP sheets are used in applications like plating and etching equipment, ventilation equipment, cookie trays, medical devices and geomembranes. [32]

2.8.3. Other forms

PP foams consist of at least two phases: PP matrix and gaseous bubbles. The structure of foams is created by expansion of a blowing agent. PP foams are used in packaging, insulation, automotive and structural applications. Density of PP foam varies within the range of 1.6-960 kg/m^3. Mechanical properties are usually linked to the density of foam. [32]

Yamaguchi *et al.* studied plywood-like structures in injection molded polypropylene plaques. The plywood-like structures of the plaques were generated with N,N'-dicyclo-hexyl-2,6-naphthalendicarboxamide nucleating agent. The plywood-like structure improved mechanical properties of polypropylene because of the crystallization and the structure. Main reason for this is that layers of the structure prevent the progress of a fracture in the material. [75]

2.9. Examples of polypropylene composites and plastics

The Finnish company Kareline Oy has developed polypropylene composites. The composites consist of PP matrix and reinforcements are wood celluloidic fibers. Wood fibers improve plastics properties and widen the temperature range where plastics can be used. All the composite brands are suitable for injection molding and extrusion. [59]

Propex is an international company which has developed Curv. Curv is self-reinforced PP composite. PP reinforcements in PP matrix improve its mechanical properties compared to pure polypropylene. Curv can be processed with thermoforming. Products manufactured with Curv include sporting goods, suitcases and the material can be also found in many cold temperature applications. [53]

Cereplast Inc. has developed bio-based plastics. Cereplast Sustainables™ are plastics which can be used to manufacture consumer goods. Cereplast Sustainables™ Hybrid Resins® consist of polypropylene and bio-based starch from sources like potatoes, wheat, tapioca or corn. One of their Hybrid Resin®: Biopropylene 50™ (CP-BIO-PP-50) is 50 % starch based and 50 % petroleum based PP plastic. The Hybrid Resins® are developed for injection molding. [51]

2.10. Health concerns related to polypropylene

Polypropylene and propylene are evaluated to Group 3 in International Agency for Research on Cancer (IARC) categories. In Group 3 materials are "Not classifiable as to its carcinogenicity to humans". [19] Polypropylene is not hazardous to health, but its processing can release volatile organic compounds (VOCs) into the air. Also some additives can be toxic or hazardous to health and require special handling during processing to protect workers and the environment. [32]

Polypropylene is a biocompatible material and therefore it has been used in medical applications, especially in drug delivery systems and in sterilizable medical packaging [10]. Biocompatible material induces a minimum degree of reaction with body tissues or body fluids and it does not impair body's normal tissue functions [6].

3. SUSTAINABLE ADVANTAGES OF POLYPROPYLENE COMPARED TO OTHER PLASTICS

Various thermoplastics and thermoset plastics are used in Nokia's mobile phones. As mentioned before, average volume of plastics in Nokia's mobile phones is almost 50 %. [67] Some plastics are more sustainable than others and in this chapter the sustainability of polypropylene is considered and compared with the sustainability of some other plastics. Sustainability may be compared from different perspectives. It is good to remember that Life Cycle Assessment (LCA) studies from two companies are usually not fully comparable even if they have used the same LCA tools.

3.1. Life cycle assessment

Life Cycle Assessment (LCA) is defined by the ISO 14040:2006 standard. "LCA considers the entire life cycle of a product, from raw material extraction and acquisition, through energy and material productions and manufacturing, to use and end of life treatment and final disposal. Through such a systematic overview and perspective, the shifting of a potential environmental burden between life cycle stages or individual processes can be identified and possibly avoided." Parameters of an LCA study are changed according to application, reason for study, audience and if the final results are public or disclosed. [23] There are three ISO standards which are designed for LCA: ISO 14041, ISO 14042 and ISO 14043. There are also ISO 14044 standard which handles LCA requirements and guidelines. [24, 69]

3.1.1. Life cycle assessment tools

There are different LCA methods: simplified LCA, detailed process-based LCA, input-output LCA and hybrid LCA. All of the methods have their advantages and disadvantages. Before making an LCA study, a proper LCA method needs to be chosen to perform the study. The proper method needs to be selected according to the focus of a study and whether the subject of the study is a product or a service. [9]

Eco-indicator 99 is one of the several impact assessment methods which can be used in the LCA [9]. The Eco-indicator assessment method enables the determination of environmental impacts. Eco-indicator 99 scores are based on the impact assessment methodology which transforms inventory table data to damage score data. This damage score data is available to users so that users can combine the needed scores. Over 200

standard indicator scores are predefined in Eco-indicator 99 for frequently used materials or methods. Eco-indicator 99 can be used with LCA software like SimaPro. The methodology is compatible with ISO 14042 requirements. [70] Another impact assessment method is Tool for the Reduction and Assessment of Chemical and environmental Impacts (TRACI). TRACI is a North American method whereas/while Eco-indicator is European method. [9] Impact assessment methods contain a quantity of impact categories. Generally used assessment methods contain 10-20 impact categories. [69]

There are LCA databases and tools that help and enable doing LCA studies which are somewhat comparable. One of these databases is Ecoinvent. Ecoinvent Centre is a Swiss competence centre that consists of Swiss Federal Institute of Technology Zürich, the Paul Scherrer Institute, the Swiss Federal Laboratories for Materials Testing and Research and the Swiss Federal Research Station Agroscope Reckenholz-Tänikon. Ecoinvent Centre offers a database where one can compare the Life Cycle Inventory (LCI) data of materials and processes. The datasets of the database are based on industrial data. The LCI data is available in EcoSpold form and it is compatible with major LCA and eco-design software tools. [54]

LCA softwares like SimaPro or GaBi are used to make LCA studies. There are various GaBi softwares available [57]. SimaPro is LCA software which includes several databases and impact assessment methods for LCA studies. For example, the Ecoinvent database is in SimaPro and it is used especially when European data is needed. The utilized assessment method needs to be selected according to the type of LCA study. In the SimaPro there are material lists of some general materials, but calculation can also be done based on custom user data. [68, 69]

3.2. Life cycle assessment studies

LCA studies can be done from several perspectives. Nokia for example has made LCA studies of whole life cycle of mobile phones, concentrated on energy consumption and greenhouse gas (GHG) emissions. These LCA studies were done according to the ISO 14044 and ISO 14040 standards. Average results from these studies can be seen in Figures 3.1. and 3.2. [65] From the figures can be seen that almost 60 % of the consumed energy was used in raw materials and component manufacturing. Next largest share was product usage of 27 %. Transportation was third with 11 % share. With the greenhouse gas emissions the three largest are the same and in the same order as with energy consumption, only the shares are different. The share of raw materials and the component manufacturing is almost 80 % of the GHG emissions, whereas product usage is 12 % and transportation is 7 %. By doing these studies Nokia has been able to minimize the environmental impact of its mobile phones [66].

Nokia performs LCA studies for new products. These studies can be found from Eco profile of the product that is explained in Chapter 6. Eco profiles can be found from Nokia’s web pages. [64]

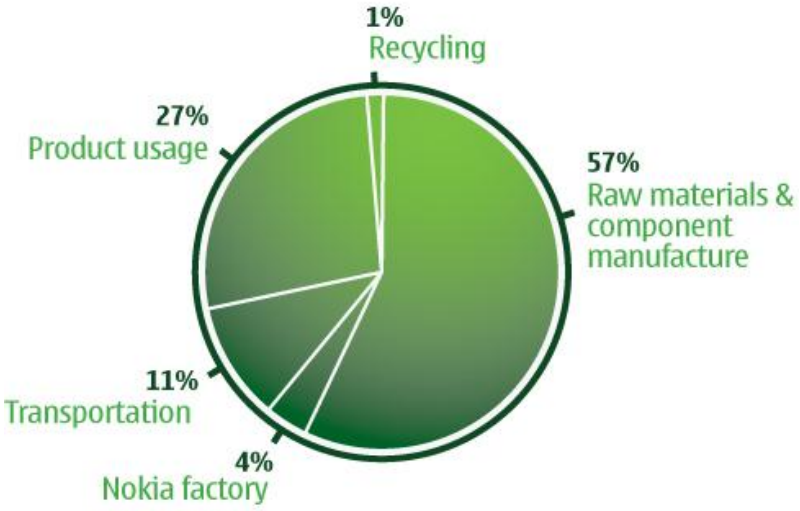


Figure 3.1. *Nokia LCA study result: Energy.[65]*

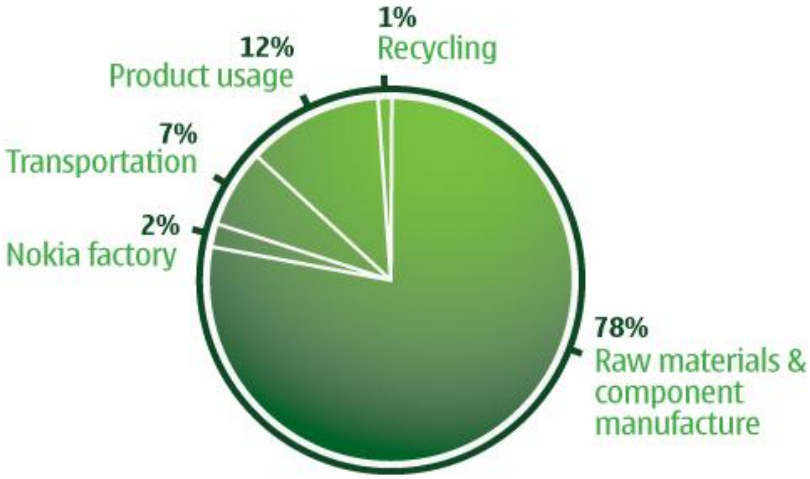


Figure 3.2. *Nokia LCA study result: Greenhouse gas emissions. [65]*

3.2.1. Green Design evaluation and life cycle assessment study

Tabone *et al.* made a study according to ISO 14040-14043 series which included an LCA and Green Design evaluations. The study was made with twelve polymers and results were compared. Ecoinvent vl1.2 database, the EPA TRACI 2 v.3.01 method and literature was used in the study. [38]

Seven out of the twelve polymers were petroleum based: PP, PET, PC, PVC, high and low density PE (HDPE and LDPE) and general purpose PS (GPPS). Four out of the twelve polymers were biopolymers, two polylactic acids (PLA) and two polyhydroxyalkanoates (PHA). The PLAs were manufactured via general process (PLA-G) and Nature Works LLC process (PLA-NW). The PHAs were manufactured from different raw materials: corn grain (PHA-G) and corn stover (PHA-S). The last polymer was hybrid bio/petroleum polymer: bio-PET (B-PET). The LCA study was

based on ten of TRACI categories: acidification, carcinogenic human health hazards, ecotoxicity, eutrophication, global warming, potential non carcinogenic human health hazards, ozone depletion, respiratory effects, smog and nonrenewable energy use (NREU). In the LCA study cradle-to-gate environmental impacts of the polymers were evaluated. The polymers were evaluated also according to Green Design metrics. The Green Design metrics were: overall atom economy, carcinogens, non-carcinogens, respiratory effects, ecotoxicity, cumulative energy demand, percent of renewable material, distance of feedstock, percent of recovery, biodegradable and price. [38]

Polypropylene was ranked as number one in the LCA part of the study. In the Green Design evaluation polypropylene was evaluated well in seven of the eleven categories. Polypropylene has the best value in three categories: non-carcinogens, respiratory effects and cumulative energy demand. In the Green Design evaluation polypropylene was ranked after biopolymers and polyethylenes. The Green Design and the LCA results were compared and the comparison of the results is in Table 3.1. [38]

Table 3.1. *The result from comparison of LCA and Green Design. Modified from [38]*

Material	LCA rank	Green Design rank
PP	1	9
HDPE	2	5
LDPE	3	7
PHA-S	4	2
GPPS	5	10
PLA-NW	6	1
PVC	7	11
PHA-G	8	2
PLA-G	9	4
PET	10	6
PC	11	12
B-PET	12	8

3.2.2. PP composites and PP comparison in life cycle assessment

Xu *et al*. made a LCA study for polypropylene wood fiber composites. In the study they compared three different PP wood composites whose fiber contents by mass were 10 %, 30 % and 50 %, respectively. They made the same comparisons with and without transportation. Another aspect in this LCA study was comparison of material service density of polypropylene and PP composites. The material service density is defined as a specific strength requirement. This is due to the fact that different materials are required in different quantities to achieve the particular mechanical load or strength. In this study the specific strength was tensile strength and the mechanical load was tensile load. [74]

The LCA study was made based on the Eco-indicator 99 assessment method and the utilized software was SimaPro. In the Eco-indicator 99 there are eleven categories of environmental impacts: carcinogens, respiratory organics, respiratory inorganics, climate change, radiation, ozone layer, ecotoxicity, acidification/eutrophication, land uses, minerals and fossil fuels. Comparison between polypropylene and composite results can be seen in Figure 3.3. Polypropylene was the dominant factor in evaluation of environmental impact of PP composite. The wood fibers of the composites have only a moderate effect to composites environmental properties. When comparing densities of the same amount of PP wood composite (30 % fibers) and polypropylene, they are 650 kg/m^3 and 900 kg/m^3, respectively. The composite is less dense than the polypropylene which causes smaller environmental impact of the composite. PP wood composites environmental effects can be reduced by specifying what characteristics the product requires. Then the product can be designed to meet the specified requirements and the environmental impact decreases. In theory the smaller amount of composite is needed than polypropylene, because of the mechanical properties of the composite. Transportation of fibers or polypropylene resins does not have great effect on the LCA of an end product. [74]

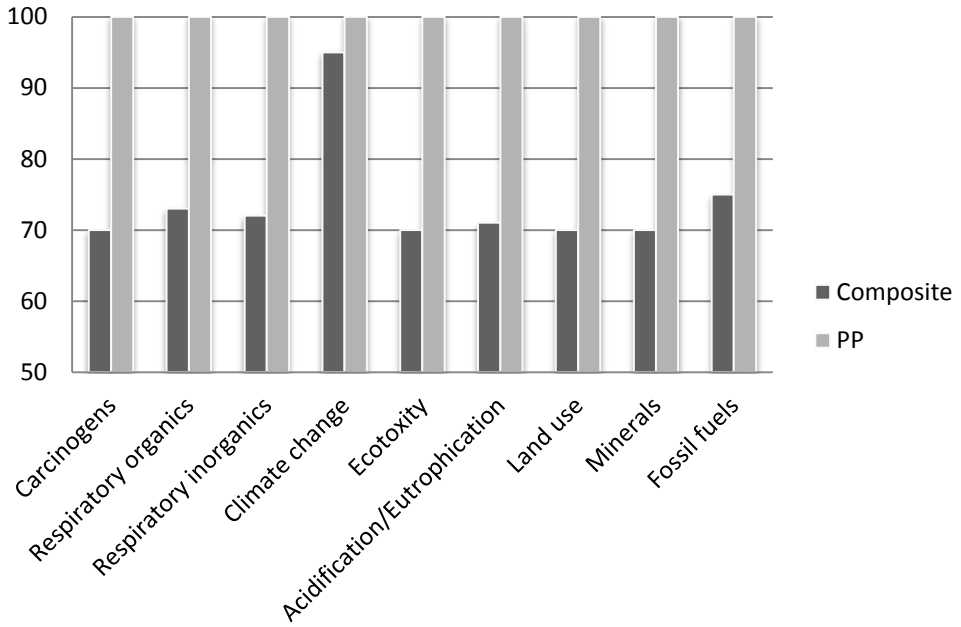


Figure 3.3. *Comparison between polypropylene and PP wood composite. Polypropylene is used as a reference for composites with value of hundred. Modified from [74]*

3.2.3. Study of substituent materials for PVC by Greenpeace

The study done by Greenpeace is about plastics toxic characteristics. It is not an accurate LCA study because it does not include raw materials and energy input. The study's main goal was to find less toxic substitutes materials for PVC. The study was done by comparing environmental and health impact of the materials in five categories:

production, additives, emissions during use, disposal and recycling. In the study polypropylene was estimated to be one of the least toxic substitutes for PVC. Toxic characteristic of the polypropylene was estimated the next smallest after bio-based polymers. Results from this study are illustrated in Figure 3.4. [15]

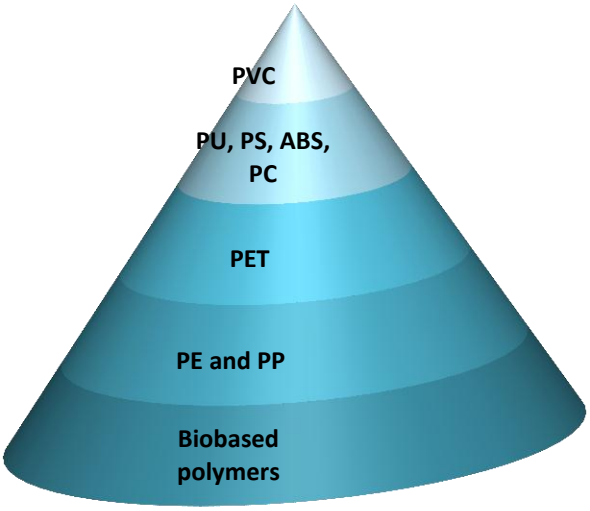


Figure 3.4. *Results of plastics toxic characteristics. More eco-friendly materials are in the bottom of the pyramid. Modified from [15]*

3.3. Life cycle assessment study for plastic

3.3.1. Introduction

An LCA study was required for the thesis. In the LCA study some plastics, which are commonly used in mobile phones, are compared with the polypropylene. The plastics were chosen according to materials used in existing mobile phones: materials of thirteen Nokia mobile phones were defined from internal documents of Nokia. Material selection was concentrated on materials which were used in mobile phone parts like covers or window and which might be replaceable with PP materials. The rather limited material selection of the used software had to be taken into account in material selection. The plastics which were selected to LCA study are: PP, PC, ABS, PMMA, two glass fiber reinforced PAs and PVC. PVC is not used in Nokia's mobile phones anymore. It was taken into this LCA study, because it also was part of other LCA studies, which are reviewed in this thesis.

In the LCA study the materials were compared according to GHG emissions and total energy consumption. The comparison is the same as Nokia has made earlier to its products.

3.3.2. Methods

The study was made with the same LCA software as Nokia uses for its LCA studies and using two Ecoinvent's databases: system and unit process. Two impact assessment methods, IPCC 2007 and Cumulative Energy Demand were used that are also same as Nokia uses. IPCC 2007 was developed in Intergovernmental Panel on Climate Change. IPCC characterizes direct Global Warming Potential (GWP) of air emissions. In the IPCC 2007 there are three different time frames, in which material is possible to be examined: 20, 100 and 500 years, in the LCA study a 100 year time frame was used. In IPCC 2007 GWP 100a results are in kilogram carbon dioxide or kilogram emissions. [68] Results of this assessment method are CO_2 equivalent. In the CO_2 equivalent all greenhouse gas emissions are converted to CO_2 based on gases global warming potential [55]. CO_2 equivalent values can be compared to carbon footprint [11] and GHG emissions values.

Cumulative Energy Demand is based on method which was published in ecoinvent 1.01. Cumulative Energy Demand calculates consumed energy in six impact categories: non-renewable fossil, non-renewable nuclear, non-renewable biomass, renewable biomass, renewable wind, solar and geothermal and renewable water. [68] Total cumulative energy for the material is obtained when all the impact categories were summed.

After the plastics were chosen, proper grades of the plastics were chosen from the alternatives provided by the software. The plastic grades used in the LCA study are:

- ABS: copolymer at plant /RER U (ABS),
- Glass fiber reinforced plastic: PA injection molding/RER U (PA-GF),
- Nylon 6: glass-filled at plant/RER U (Nylon 6-GF),
- PC at plant/RER U (PC),
- PMMA sheet at plant/RER U (PMMA sheet),
- PP granulate at plant/RER U (PP) and
- PVC granulate at plant/RER U (PVC).

After selecting the materials the software was used to calculate cumulative energy demand and GHG emissions. These are materials that were already in the list in the software and they are not the specific plastic grades which are used in mobile phones. The values of the Ecoinvent are average values of Europe for these plastics. By choosing the plastics from the same database, their comparability is better. All the results are calculated to the one kilogram of the material. Biopolypropylene was not part of this LCA study because in the database was not data for it.

3.3.3. Greenhouse gas emissions results

Mobile phones plastics GHG emissions results are presented in Figure 3.5. The used assessment method was IPCC 2007 GWP 100a. Results are kilograms of CO_2 equivalents to one kilogram of the material. From Figure 3.5. it can be seen, that GHG

emissions of PP are 1.97 kilograms which is the smallest of the comparison. GHG emissions of PA-GF are 8.79 kilograms which is the largest and it is almost seven units larger than value of PP. ABS and PC are usually used in mobile phones as a blend, but there was not ABS/PC blends in the lists. GHG emissions of both of the two plastics are separately larger than GHG emissions of PP. Also GHG emissions of the PMMA sheets are clearly larger than PP's. Although the PMMA is sheet and there are reinforcements in PA-GF and Nylon 6-GF GHG emissions of PC are third largest after PA-GF and PMMA sheet. In fact GHG emission values of four grades: PA-GF, PMMA sheet, PC and Nylon 6-GF, are over 7 kilograms while remaining three: PP, PVC and ABS values are less than 5 kilograms. When comparing GHG emissions of PP to PC, which has value of 7.78 kilograms, the difference is almost six kilograms.

When comparing these values it is good to remember that the plastic grades are not the specific grades which are used in mobile phones and there is variation in the forms of plastics. PMMA plastic is sheets whereas the other plastics are in some other form. It is also good to remember, that reinforced plastics results are affecting also the reinforcement like glass fibers in the PA-GF.

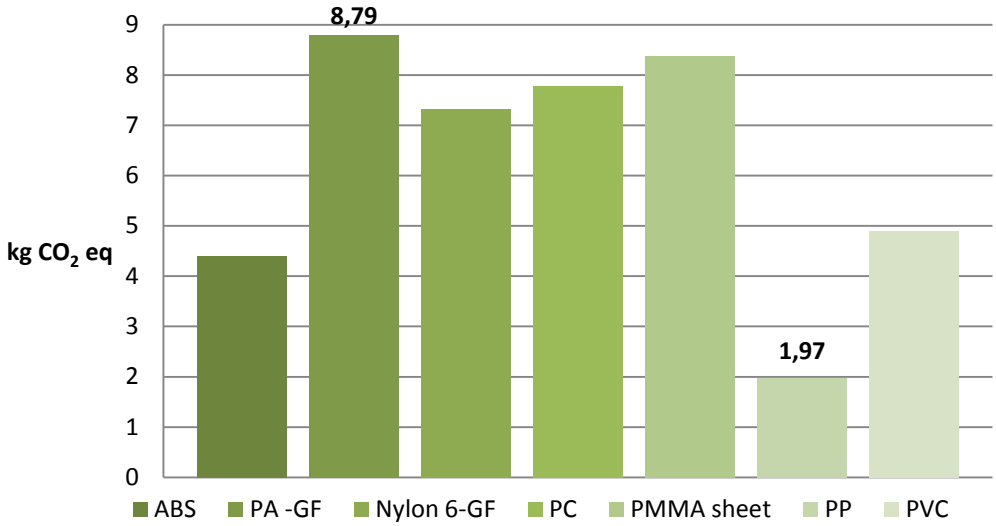


Figure 3.5. *GHG emissions results of the plastics LCA study.*

3.3.4. Energy consumption results

In energy consumption the used assessment method was Cumulative Energy Demand. As mentioned above in the assessment method the energy consumption consists of six energy categories. In the results, the energy categories are specified and separated. In the separated results it is possible to compare the consumption of energy sources directly. In Table 3.2. the energy categories are separated to polypropylene. From the table it can be seen that the total amount of consumed energy to produce one kilogram of polypropylene is 75.12 MJ. From Table 3.2. is possible to also see that the most of the consumed energy is from non-renewable energy sources. In fact 70.41 MJ of energy

is obtained from non-renewable fossil, which is about 94 % of the total energy amount whereas the other two non-renewable sources are remarkably less used around 5 MJ. Furthermore, from renewable sources less than 1 MJ of energy is obtained. The trend was similar to all of the plastics of the study: the most of the consumed energy is obtained from the non-renewable energy sources. However, it is good to remember that in the end the consumed energy depends on what energy source is used at that time.

Table 3.2. *Polypropylene specific energy consumption by energy sources.*

Impact category	Energy	
Non-renewable, fossil	70.41	MJ
Non-renewable, nuclear	4.23	MJ
Non-renewable, biomass	7.29E-08	MJ
Renewable, biomass	0.18	MJ
Renewable, wind, solar, geothermal	1.42E-04	MJ
Renewable, water	0.30	MJ
Total	75.12	MJ

Results of the energy consumption section of the LCA study are illustrated in Figure 3.6. *Energy consumption results of the plastics LCA study*The results are to one kilogram of material. Energy consumption of PP was 75.12 MJ which is the lowest in the LCA study. Comparing energy consumptions of PP and the most consuming PA-GF the difference is over 70 MJ. While both PA-GF and Nylon 6-GF are glass fiber reinforced polyamide plastics their energy consumption has remarkable difference, while PA-GF consumes 147.81 MJ and for the Nylon 6-GF value is 106.17 MJ. When energy consumption of PC (107.51 MJ) and the Nylon 6-GF are compared, energy consumptions are almost the same, although only Nylon 6-GF has reinforcements. When energy consumption values are compared it is good to remember the same things as with the GHG emissions results.

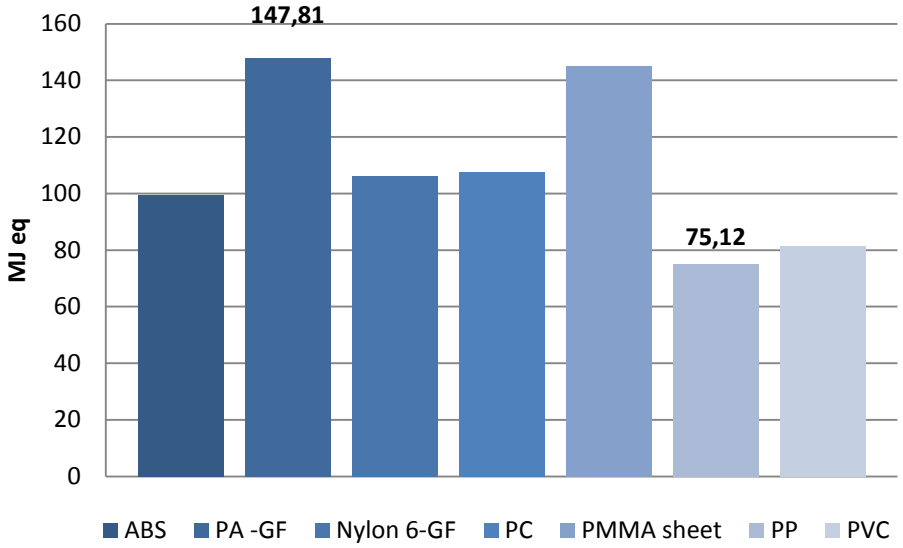


Figure 3.6. *Energy consumption results of the plastics LCA study, the results include many energy sources.*

3.3.5. Conclusion

Polypropylene performed well in the LCA study. With both assessment methods it had the lowest value which in this case was the best. Even though, polypropylene is the better choice for an ecological point of view, in applications like mobile phone, materials need to be chosen according to required mechanical properties. After the required mechanical properties are achieved then sustainability and the environment needs to be taken into account in material selection. Although, PVC did quite well in the LCA study it has other unwanted characteristics, like toxicity, which is why Nokia no longer uses it in products. Therefore also health issues of the material need to be observed before usage.

When polypropylene is considered from the LCA studies point of view, it is good choice to replace plastic materials which are used today in the mobile phones, for example, in covers. Polypropylene has smaller environmental impact than other plastics of the study.

When considering polypropylene materials to mobile phone applications it is good to remember that required mechanical properties may not fulfilled with pure polypropylene. The mechanical properties of PP composites are better than pure polypropylene and therefore, they might be better alternatives to materials which are used today in mobile phones. At the same time composites and reinforcements change mechanical properties they also change energy consumption and GHG emissions of materials. When using PP composites or other PP materials with added reinforcements or fillers, they need to be taken into account in LCA studies. If differences in these materials need to be defined, it is necessary to make a new LCA study. Like Xu *et al.* noted in their study, smaller amount of composites are needed to achieve same mechanical properties than pure material [74].

4. REVIEW OF BIOPOLYPROPYLENE AND BIOREFINERY CONCEPTS

In this chapter is discussed how bioplastic or biopolypropylene is defined. There is also review of biorefinery concept, because it is linked to manufacture of bioplastic. The chapter also introduces one possibility of sustainable biorefinery raw material. Furthermore, it is good to remember, that sustainable raw materials cannot be used as a food source. Therefore, it is important to study new raw material options from which could be replaced for example corn.

4.1. Bioplastic

The concept of bio-based plastics or bioplastics varies. How large the variety is, depends on how the bioplastic is specified. Bioplastics are plastics which are manufactured from biomass sources. Furthermore, they provide a carbon neutral and less fossil fuel dependent options for conventional plastics. [40]

Plastic manufactured from renewable sources has an identical chemical structure as the same plastic that is manufactured from oil and also mechanical properties of plastics are similar. However, greenhouse gas emissions of bioplastics are smaller than those of conventional plastics and in addition their prices are not linked to market price of the raw oil. [42]

2007 biodegradable plastics were produced worldwide approximately 350 000 tons [37]. Currently there are on the market bioplastics in which natural biopolymers like starch or cellulose have been added. One of these materials is Cereplast Biopropylene 50™, introduced in Section 2.9. which is half petroleum based and half starch based plastic [51]. The amount of bio-based material reduces the amount of needed oil-based polymer in plastic. On the market are also bioplastic which are manufactured from biopolymers, like Cereplast Compostable, which are biodegradable and compostable plastics [50].

When bio-based materials are mixed with conventional plastic, it affects properties of plastic and processing procedures. Furthermore, when talking about bioplastics it is good to remember that all bio-based materials are not biodegradable [37]. Although, biopolymer can be biodegradable or non-biodegradable the conventional polymer is usually non-biodegradable [37]. Chemical structure affects biodegradability of the materials more than what it has been made of.

4.2. Biopolypropylene

There are no totally bio-based polypropylenes yet on the market. However, there are various routes to produce propene from raw materials such as corn, biomass and vegetable oil. This propene is referred as green propene. Green propene can be produced by sugar fermentation, gasification or fluid catalytic cracking unit. [52] Furthermore, there is research and development to produce green polypropylene.

Braskem is a Brazilian petrochemical company who has been able to produce biopolyolefins from sugarcane. So far, they have commercially produced biopolyethylene, which is called green polyethylene. The green polyethylene is manufactured from bioethanol which is generated from sugarcane. In fall 2010 Braskem opened a green ethylene plant. [46] Green polypropylene was introduced in laboratories during 2008. Like green polyethylene, green polypropylene is also completely made of renewable resources like sugarcane. Braskem is doing research to evolve green polypropylene production into industrial scale. [47] In 2010 the company concluded basic engineering studies about green polypropylene plant. The operational startup of the plant is expected to be in 2013. [45]

4.3. Biorefinery

In petroleum refinery energy, fuels and chemicals are produced from petroleum. Biorefinery is analogous to the petroleum refinery. As a starting material it uses biomass from agricultural or forestry residues. Agricultural residues can be used like non-edible parts of corn or wheat. [8] Forestry residues could be saw dust, lignin, and recycled or rejected pulp [11]. Biofuels products from biorefinery are similar to petroleum refinery products so they can be used in similar way. [8] There are at least three different biorefinery systems: whole-crop biorefinery, green biorefinery and lignocelluloses feedstock (LCF) biorefinery. Whole crop biorefineries use cereals or maize as raw material. In the green biorefineries raw materials are naturally wet biomass like green grass or immature cereal. The raw materials of LCF biorefineries are naturally dry biomass such as cellulose-containing biomass and waste. [26]

Biorefineries process and convert biological raw materials to valuable products. Some of the products cannot be processed from petroleum refineries. [26] Biorefinery products can be divided into two groups: material products and energy products. Energy products are produced because of their energy content. They are used to produce electricity, heat or power for transport. Material products are produced because of their chemical or physical properties. [7] The main goal in biorefinery is to produce bio-based fuels like bioethanol, biodiesel and biogas. For the meantime bio-fuels are mainly produced from food crops such as wheat and corn. In the future, second generation biofuels are produced from non-food crops or forestry. [7] Figure 4.1 shows a schematic of the III generation biorefinery. One future raw material possibility might be cellulose,

which can be to depolymerised to glucose and then used as base substance to fuels, chemicals and materials [11].

Bioethanol is an ethyl alcohol which can also be produced in traditional way from hydrocarbons. Bioethanol is produced in a fermenter from six carbon sugars like glucose or sucrose. Sugars are gathered from biomass in agriculture or waste products. [7]

It is possible to derive the same chemicals in biorefinery from biomass than in oil-refinery from raw-oil. When chemicals are derived from biomass the yield is lower and the cost higher than in deriving chemicals from oil. [7]

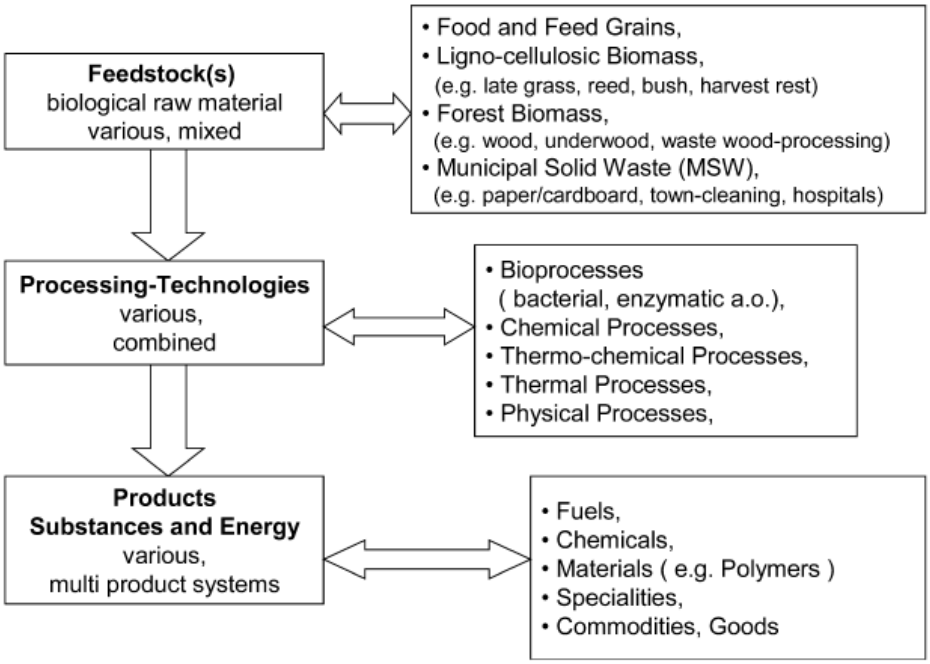


Figure 4.1. *Basic principle of phase III biorefinery. [26]*

4.4. Ligno-Cellulose

Ligno-Cellulose might be used in future as raw material in biorefineries. Ligno-Cellulosic biomass is cellulose, hemi-cellulose and lignin. They can be divided to soft and hard biomass. The soft biomass are less lignin containing biomass like office paper or corn stove whereas the hard biomass is more lignin containing biomass like wood materials. Different carbohydrate and non-carbohydrate that could be used in biorefinery may be gathered from these biomasses. To get these materials into use, effective enough glycation technology is needed. There is on-going research in that area. [40]

Lignin is an irregular polyphenolic polymer that can be found from cell wall of plant cells. Generally 27-33 % of biomass of softwood is lignin, hardwood 18-25 % and grass 17-24 %. [35] Lignin from different sources have different chemical structures. Softwood lignins are usually classified as guaiacyl lignin, whereas hardwood and grass

lignins are classified as guaiacyl–syringyl lignins. Although, hardwood and grass lignins are classified similarly they are not structurally identical. [30]

Presently there are still some problems in exploiting lignin. One of the main issues is the fragmentation of it. [35] It is possible to break the chemical structures of lignins in several ways depending what is the wanted end product [30].

In the existing lignocelluloses-based biorefineries lignin is not exploited completely, although lignin could be converted into precursors or platform chemicals. These chemicals could replace oil as chemicals raw material and even in polymer and bio-based plastic production. [11]

5. MARKET SURVEY AND INDUSTRY TRENDS

The price of plastics changes continuously and also plastic markets are changing, as new renewable or greener plastics are emerging. These new plastics change the market shares and force old plastics to evolve towards newer technologies. In the future petrochemical plastics need to change in order to fulfill the more ecological demands of the markets.

5.1. Present situation

Polypropylene is one of the most used plastics along with polyethylene and PVC [25]. PVC usage is going to decrease though, because of its health hazards. Furthermore, PC is also one of the plastics whose usage has been restricted because of bisphenol A substance in the plastic. For example, EU Commission tightens 2006 directive by directive 2011/8/EU in products for infants like feeding bottles [21]. These kinds of restrictions are changing the habits of the consumers with plastics as they also increase the consumers' knowledge of differences in plastic and their health concerns.

5.1.1. Market

The mass production plastics have 80 % market share in Finland. Polyolefins have 80 % of the market share, in 2007 the market share of polypropylene was 19 %. This amount is approximately 81 700 tons. The mass production plastics prices are tied to the price of raw oil. At the turn of the millennium prices of all plastics have risen. Price of polypropylene has risen along with other mass production plastics in the 2000's. The prices have risen at a similar rate so that the difference between the price of plastics has stayed the same. [25]

Prices of plastics are in constant change as are also the plastics internecine placings. Figures 5.1. and 5.2. show the daily variation of the price of polypropylene. Comparing prices of plastics, especially volume prices €/dm^3 and €/kg it can be seen that plastics' €/dm^3 and €/kg vary greatly. Järvinen presents in Uusi muovitieto good figures of volume prices of mass production plastics and engineering plastics in 2008. Prices of some plastics are gathered in Table 5.1. Price by volume of mass production plastic varied approximately from 1.2 to 1.8 €/dm^3 while variation of price by mass was approximately from 1.1 to 1.4 €/kg. Price by volume of engineering plastic varied between 3.0 and 4.8 €/dm^3 and price by mass variation was between 2.7-3.6 €/kg. [25]. Some remarkable differences in prices of mass production plastics and engineering

plastics may be observed. As can be seen from Table 5.1. difference of PC+GF price by volume and price by mass is nearly 1 euro.

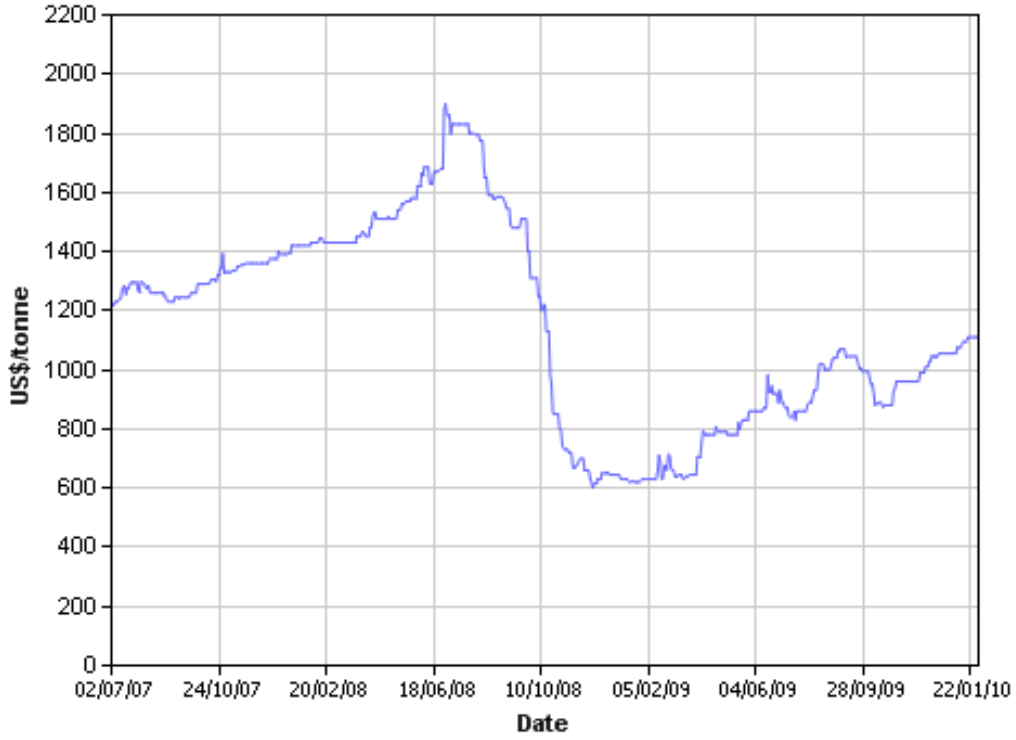


Figure 5.1. *Global price graph of polypropylene approximately during 2.5 years, Prices are for buyer. [60]*

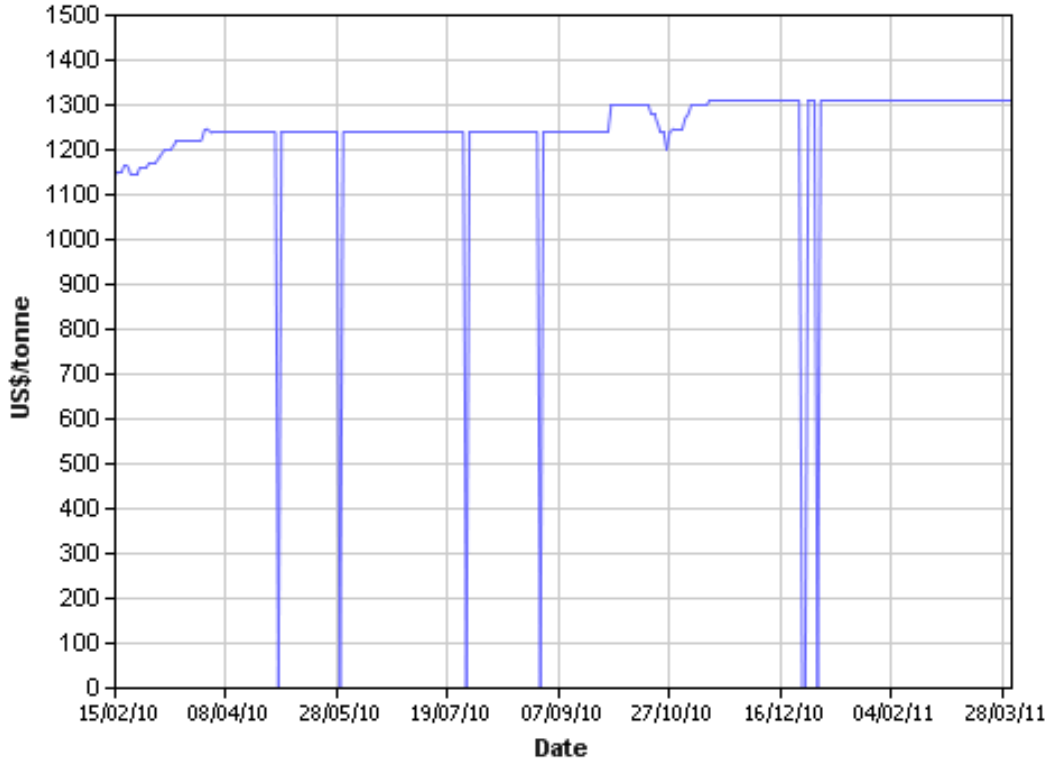


Figure 5.2. *Global price graph of polypropylene from the 15.2.2010 to the end of March 2011. Prices are trade weighted average price. [60]*

Table 5.1. *Some volume prices of plastics. [25]*

Polymer	€/dm^3	€/kg
PP	1.2	1.3
PET	1.8	1.3
PA6	3.0	2.7
PC+GF	4.5	3.6

Polypropylene is one of the most versatile bulk polymers and it has secured its position in a wide variety of uses in industry and household goods. Injection molded PP, can be used in toys, luggage and electrical appliances as well as automotive sector, to name but a few. PP films can be found in applications like packaging of sweets and electronic films. PP fibers are utilized for example in clothing, carpets and ropes. Wires, cables, pipes and conduits can be made from polypropylene by extruding. [25, 32, 58]

Because of versatile properties of the polypropylenes it can be used as a substitute material to metals, paper, glass and other plastics. In fact polypropylene has increased its markets share costs over other plastics like PS, ABS and PVC. [1]

PP plastics are the most used plastic in automotive industry, every car has about 60 kilograms of PP parts [25]. The PP plastics used in automotives are usually compounded with glass fiber or talc. Different PP plastics may be used in car applications such as bumpers, door post cladding and pockets and textile surfaces. [25, 32] In January 2011 Borealis and Peugeot announced that front grill of Peugeot car model 206+ is going to be made of Borealis PP plastic Daplen EH104AE-0515 [44]. In 2008 Toyota Motor Company has also announced that they aim to replace PVC, ABS and polyurethane (PU) with polypropylene made from renewable sources in the future. Their near future goal is to replace 20 % of plastics in automobiles with bio-plastics by 2015. [11]

5.1.2. Industry trends

Production processes of polypropylene have been licensed. There are only few different licenses and most of the large polypropylene manufacturers have their own processing methods. LyondellBasell's Spheripol and Spherizone are licensed technologies to manufacture polypropylene. In 2003-2009 over 40 % of polypropylene was produced by LyondellBasell' processes. [1]

In Europe production capacity of the polypropylene was about 11 800 million kilograms in 2007. The biggest manufacturer in Europe that year was Basell (now LyondellBasell) and its market share was 28 %. The second biggest producer was Borealis with a market share of 17 %. [25] Polypropylene producers are located around the world. Producers like Lyondellbasell, Exxon Mobil and Borealis are big international companies that have plastic refinery plants in several countries all over the globe. [43, 56, 61]

5.2. In the future

New kinds of polypropylenes will to replace engineering plastics and other materials such as glass or metal. This shift is going to increase the market share of polypropylene. [32] Role of polypropylene in automotive industry will increase, partly due to its light weight. Polypropylene is lighter than many other plastics which means lighter parts and thus weight reduction. [25] By reducing the weight of cars it is possible to achieve fuel saving and also reduce CO_2 emissions.

5.2.1. Industry trends

In the next five years worldwide capacity of polypropylene is predicted to rise to 71.5 million m.t. per year. This means a growth of more than 10 million m.t. per year. Growth demand of polypropylene is predicted to be 5-10 % per year in 2010-2012. [1]

Polypropylene producers have increased their operational efficiency and in the future this trend will continue. Producers will close or reduce less efficient polypropylene producing plants and centralize polypropylene production to more efficient plants. At the same time producers like LyondellBasell and ExxonMobil Chemical are going to improve their own polymerization processes to meet current demands. [1]

Polypropylene manufacturers have centralized and developed their refineries and this trend is most likely to continue. This may cause change to locations of suppliers as new places might become more inciting. [1] In the future, different eco-friendly polypropylenes will also change the markets. Good examples of this kind of polypropylene are green polypropylene of Braskem, or PP blends with biomaterials from other manufacturers, for example grades of Cereplast [46, 51]. Furthermore, Braskem plan to open the biopolypropylene plant was mentioned before [45], this will hopefully enhance development of other manufacturers towards biopolypropylene and other bioplastics.

6. PLASTICS IN MOBILE PHONE APPLICATIONS OF NOKIA

In this chapter currently used mobile phone materials are discussed and some of their properties are compared. There are also some properties of biopolypropylene that can be compared to the properties of the currently utilized plastics.

6.1. Current materials used in Nokia mobile devices

As mentioned before, almost 50 percent of mobile phones consist of plastics. Mobile phone covers are manufactured from plastics or metals. Because covers are one of the largest individual parts of the phone, the change of material reduces notably amount of plastics in the materials used in the phone. Furthermore, generally it can be said that metals are heavier than plastics. Therefore, cover material has also a rather remarkable affect the weight of the mobile phones.

Presently PP plastics are used in Nokia mobile devices in small amounts, but not in structural parts like covers or frames. Some plastics which are utilized in Nokia devices are: PC+GF, ABS+PC blend, PMMA, poly(*p*-phenylene sulfide) (PPS), polybutylene terephthalate (PBT) and PA-GF. Especially PC+GF, ABS+PC blend, PMMA and PA-GF are utilized in structural parts of mobile devices. [39] Figure 6.1. illustrates where some of these plastics are utilized in Nokia mobile phones. [10]

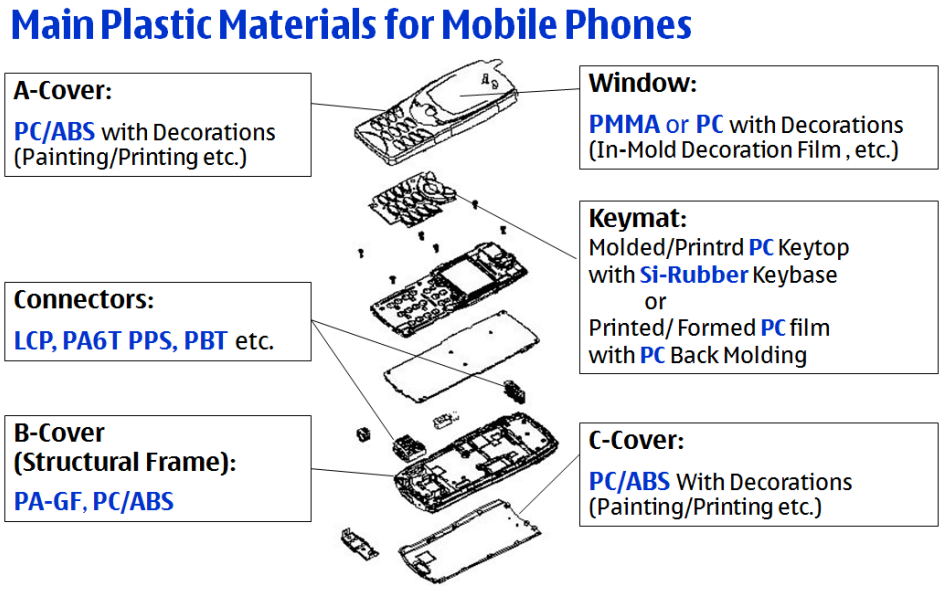


Figure 6.1. *Utilization of plastics in mobile phones. [39]*

6.1.1. Eco profiles

Since May 2010, all published products have Eco profiles on the Internet. For products, published between 2001 and May 2010 Nokia has published Eco Declarations which are also available on the webpage of Nokia. Eco Declaration contains "basic information on the environmental attributes of the product covering material use, energy efficiency, packaging, disassembly and recycling". [64] From Eco profile one can find environmental features, materials used, restricted substances, energy consumption, packaging, recycling and environmental impact of the product. [20]

Under "Used materials", the materials are categorized into five groups, from which four are for material groups and one is for battery that is handled as a unity. The groups are: metals (for example stainless steel, copper and precious metals), plastics, ceramic materials (glass and other ceramics), others (non-metals such as silicon and other materials like glue) and battery (for example lithium, cobalt). There is also a material pie chart from which is easy to see how materials are approximately used in the phone. The material pie chart is divided into sections according to material category weight share.

Environmental impact category includes LCA study results of GHG emissions and energy consumption. For example, a material pie in Figure 6.2. is from Nokia C7-00 Eco profile. Figure 6.2. shows that 32 % of the phone is plastic materials. [20] However, total plastic content of mobile phone is little more than 32 %, because there is also some amount of plastics in battery.

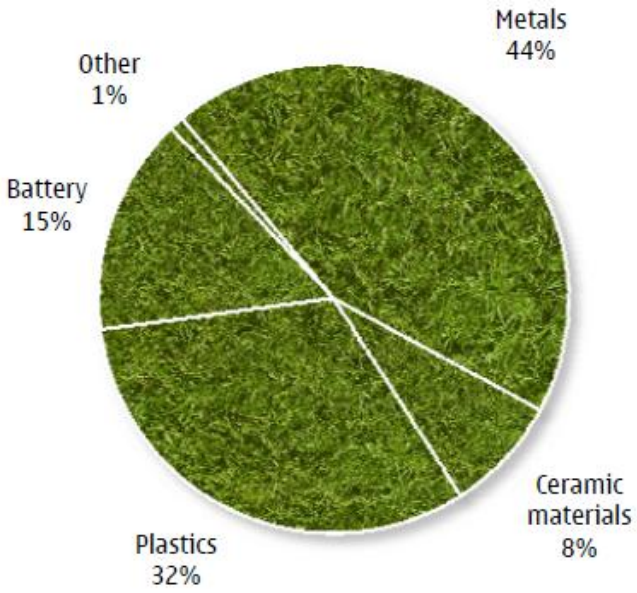


Figure 6.2. *Material categories of Nokia C7-00 mobile device. [20]*

6.2. Properties of currently used plastics

The chemical structure of the polymer is the base of its properties. Polyethylene is the simplest polymer, it consists of carbon backbone and hydrogens which are attached to the carbons. Large side groups or other atoms in addition to carbon in the polymer backbone are affecting to rigidity of polymer backbone and from that polymer chain folding and polymers crystallinity and properties. [10] As Figure 2.1. illustrates polypropylene has methylene side group which behaves like a pendant. Besides the pendant the mer unit of polypropylene is quite simple as it can be seen in Figure 2.3. whereas, a mer unit of polycarbonate is rather complicated while it contains oxygen atoms and aromatic rings. Backbones of polyamide polymers contain nitrogen atoms. Furthermore, their mer units are rather complicated. [6, 10] The mer units of polyamide (Nylon 6-6) and polycarbonate are illustrated in Figure 6.3.

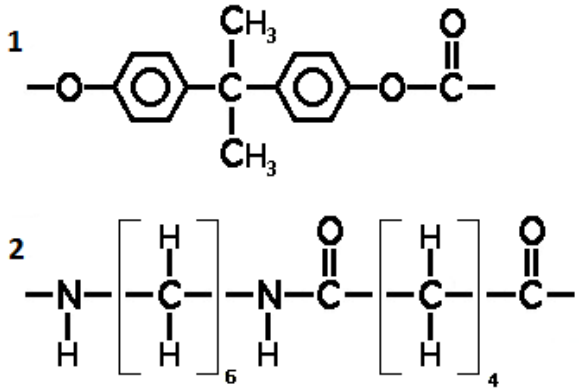


Figure 6.3. *1. Mer unit of polycarbonate 2. Mer unit of aliphatic PA (Nylon 6-6). Modified from [6]*

Table 6.1. presents some properties of some polymers which are used in mobile phones: PC, PMMA, ABS, Nylon-6 and Nylon-6,6, and polypropylene. Generally used Nylon-6 and Nylon-6,6 are aliphatic polyamides [10]. Polyethylene is not used in structural parts of mobile phones either but it is there for comparison. All values are from literature, so they are not exact values to a specific plastic grade. In mobile devices PC and ABS are frequently used as a blended material. In Table 6.1. values are for pure materials. As it can be seen from Table 6.1. polymers properties may vary within the limits depending on some properties of polymers like tacticity and even polymerization method. For example, when mechanical properties of polypropylene and polycarbonate are compared, it can be seen that tensile modulus of polycarbonate is somewhat larger than polypropylene. Other properties of polycarbonate like yield and tensile strengths are clearly larger than values of polypropylene. However, heat-deflection temperature of polypropylene is the largest of these plastics. Although T_m of polypropylenes is not as high as some other plastics, 177 °C is enough for everyday applications.

Table 6.1. *Some properties of commercial polymers. Modified from[6, 10]*

Polymer	**Tensile Modulus (GPa)**	**Yield Strength (MPa)**	**Tensile Strength (MPa)**	**Stress at break (yield) (MPa)**	**Elongation at Break (%)**	**Izod Impact Strength (J/m)**	**Density (g/cm^3)**	**T_g (°C)**	**T_m (°C)**	**Heat-deflection temperature (°C at 455 kPa)**
PP	1.4-1.55	31-37.2	31-41.4	33	100-600	80	0.9-0.95	(-10)-(-18)	177	225-250
PC	2.5	62.1	62.8-72.4	60	110-150	800	1.2-1.31	141-150	227	138
PE (high density)	1.06-1.09	26.2-33.1	22.1-31.0	10-30*	10-1200	130-170*	0.91-1*	(-120)*	98-135*	60-88
Nylon-6	1.9	-	-	75	300	-	1.08-1.23	46-60	223	150-185**
Nylon-6,6	1.58-3.80	44.8-82.8	75.9-94.5	80	15-300	110	1.07-1.24	45-57	265	180-240**
PMMA	2.24-3.24	53.8-73.1	48.3-72.4	65	2.0-5.5	27	1.17-1.23	105-126	160	-
ABS	2.07-2.76	-	41.4-51.7	-	5-25	-	1.03-1.06***	-	-	102-107
PPS	2.14	-	-	-	60	-	1.29***	-	-	200-204

* All grades

** Moisture conditioned

*** Specific gravity

Järvinen has made in the Uusi Muovitieto some good comparison of mechanical properties of plastics. In the book some mechanical properties of PP and PC+ABS are compared. It may be observed, that notched impact strength (+23 °C) of PP is approximately 10 KJ/m^2 and Young's modulus is approximately 1 300 MPa. PC+ABS values are respectively approximately 40 KJ/m^2 and 2 300 MPa. Furthermore, also notched impact strength (-20 °C) of plastics was observed, it was approximately 6 KJ/m^2 for PP and 18 KJ/m^2 for PC+ABS. [25] As from these values can be seen, notched impact strength at +23 °C of PC+ABS is approximately four times larger and at temperature -20 °C is about three times higher than value of the PP. Also Young's modulus of PC+ABS is clearly higher than PP's.

As it can be seen from Table 6.1., and comparison with some properties of the PC+ABS mechanical properties of polypropylene do not compare, but as the LCA studies showed, polypropylene has lower environmental impact than the most of these engineering plastics. Mechanical properties of polypropylenes may be improved by adding reinforcements. As Xu *et al.* showed, reinforcements do not affect greatly to environmental impact of reinforced plastic [74].

6.3. Biopolypropylene

Presently biopolypropylenes that are available on the market like Cereplast Hybrid Resins mechanical properties are not high enough for this kind of use. For example, tensile strength of biopolypropylene is 17.4 MPa whereas tensile strength of polypropylene is 31 MPa and heat deflection temperature is for biopolypropylene 74 °C and polypropylene 225 °C. [16] Some properties of biopolypropylene are shown in Table 6.2. Values in the table are one of Cereplast grades and are from manufacturer datasheet. However, one major reason for these weak mechanical properties is the starch in plastic.

Table 6.2. *Some properties of a biopolypropylene grade that includes starch. [16]*

	Biopolypropylene
Tensile Strength	17.4 MPa
Tensile Elongation	10 %
Tensile Modulus	1.07 GPa
Flexural Modulus	758 MPa
Notched Izod Impact Strength (23 °C)	37.4 J/m
Temperature Deflection Under Load (450 kPa)	74 °C
Density	1.05

Mechanical properties of biopolypropylene are equivalent to conventional polypropylene and they can be processed with various industrial technologies [37] However, further development is still needed before biopolypropylene could be used in

more demanding applications like mobile devices. Furthermore, with reinforcements mechanical properties of biopolypropylenes may be improved enabling their use in demanding applications.

7. TESTING OF THE SELECTED PP PLASTICS

The first Section in this chapter describes how materials were chosen for testing. Also some material selection tools are introduced. After the selection of materials their injection moldability was tested. Properties of the plastics and how they behave while they are injection molded are tested with two injection molding machines.

7.1. Introduction

After the literature research it can be said the properties of polypropylenes are quite versatile. Chemical resistance of polypropylene is good and it can be processed with various techniques. However, mechanical properties of polypropylenes can be quite limited. Furthermore, these properties can be improved with fillers and reinforcements.

As mentioned, before polymerization of polypropylene affects the properties of polypropylene. However, polymerization method is seldom mentioned in manufacturer datasheets. Therefore, polymerization method is not taken into account when selecting materials.

7.2. Materials selection

There are several polypropylene manufacturers on the market and they have various PP plastic grades. When choosing polypropylene grade to a specific application properties of the grade need to meet the requirements of processing and the end product. Plastic parts of mobile phones such as covers, are usually injection molded so grades need to be injection moldable. There are also other requirements depending on the part.

The required mechanical properties were studied using existing mobile phones and product requirements of Nokia. Most of the study was made from internal documents. 13 pieces of Nokia mobile phones materials of A, B and C covers were studied from the documents. A, B and C covers are illustrated in Figure 6.1. The covers were made from various plastics or metals, and some of the mobile phones were disassembled as well so that their plastic parts could be examined closer. After disassembling the phones, materials of their covers were checked from the internal document. Plastic materials that might be replaceable with polypropylene plastics were PC+GF, PC+ABS blend, PMMA and various PAs.

Actual material selection was made with the help of Computer Aided Material Preselection by Uniform Standards (CAMPUS), MatWeb and Material Data Center. They are databases that help in selecting polymer grade. CAMPUS is a program that can be loaded to a computer or purchased. MatWeb and Material Data Center are

internet services which need registration to get full access to datasheets. [62, 63] CAMPUS is a material information system for the plastic industry. In CAMPUS there are datasheets of plastics of several manufacturers organized in a way that they can be compared. All datasheets do not contain the same information and latest information needs to be confirmed from the manufacturer. [48] Before comparing the materials some preselection was made to limit the comparison only to injection moldable PP grades.

Mobile phone cover B material PA+GF plastic was compared in CAMPUS with PP plastics. When tensile moduli of materials were compared, pure PP plastics did not achieve the required level. However, PP plastics with glass fiber reinforcements succeeded quite well.

Material of covers A and C, PC+ABS, was compared to PP grades. PC+ABS material properties were observed from Material Data Center and they were compared in CAMPUS, Material Data Center and MatWeb with properties of PP plastics. When comparison was done only on the tensile modulus there were several PP plastic alternatives to substitute the PC+ABS and some of alternatives were pure PP plastics. Furthermore, when the comparison was done with required impact strength (Charpy or Izod) it reduced the amount of possible PP plastics quite substantially and limited pure PP plastics. However, mechanical properties of some of the PP plastics with mineral filler or glass fiber reinforcements were good enough.

Operating temperature of plastics can seldom be found from datasheets. However, a datasheet may present various temperature related tests like Vicat softening temperature and heat deflection temperature, which are also important to know.

When considering alternatives to window material of mobile phones, the restricting properties are transparency and mechanical properties of material. There are transparent PP plastics but their mechanical properties were quite unsatisfactory.

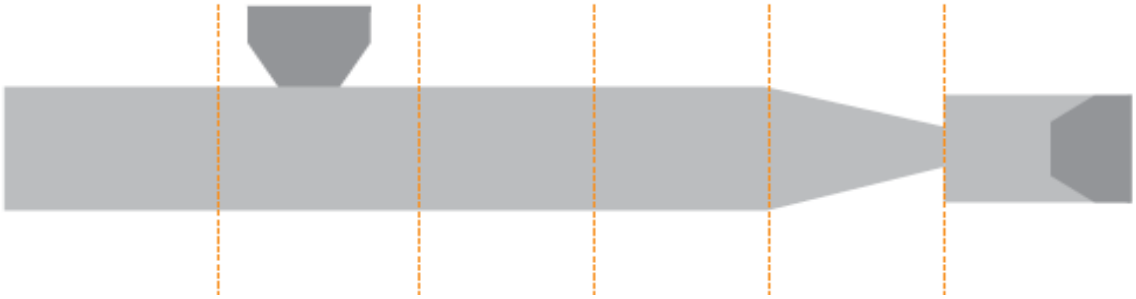
After the material selection process four plastics were selected for the testing: Borealis' MD2060U and Nepol GB21HP, Ticona's CELSTRAN PP-GF30-02 and Albis' Altech PP-B A 2020/150 GF 20 CP. None of the materials are pure; MD2060U contains mineral filler and the other three plastics have glass fiber reinforcements because mechanical properties of a pure plastic were not high enough to meet the requirements.

Unfortunately due to circumstances the selected materials were not available so the materials needed to be reselected. In the end PP plastics that were tested were: two chemically coupled glass fiber reinforced 30 % and 40 % PP plastics and a PP plastic with 40 % carbonate calcium mineral filler. The plastics were manufactured by So.F.Ter Spa, Italy and the plastic grades were Polifor L6 GF/40 Naturale (Lotto: 2480406), Polifor L6 GF/30 Naturale (Lotto: 25395Q7/2) and Polifor 12 Ca/40 Naturale (Lotto: 2476706). Hence PP plastic grades are called respectively PP GF/40, PP GF/30 and PP Ca/40. [71]

7.3. Processing

After the selection, materials were processed so they could be tested. In this case materials were injection molded to mobile phone covers. Some of the testing was also done during the molding process. The injection molding was executed by subcontractor of Nokia, Lite-On Mobile in Vantaa by Mikko Silvennoinen. Mikko Silvennoinen also helped with the analysis of the results.

Two injection molding machines: ENGEL (Type: ES 200/80 Number: 43380, Year of construction 2000, clamping force 80 ton and screw diameter 25 mm) and Fanuc Roboshot α-100 *i* A (Type A078-1020-B 001 #E30, Serial Number: A99780573, Date 1999-07, clamping force 1 000 ton and screw diameter 26 mm) were used. Injection molding process is described in Subsection 2.7.1. Injection moldability of materials was tested with the Fanuc machine, where ENGEL injection molding machine was used to mold the test pieces for testing. Figure 7.1. illustrates Polifor PP plastics, with fillers and reinforcements, injection molding guide temperature ranges and their zones in an injection molding machine. Reinforced PP GF/30 and GF/40 all temperatures were at ranges. PP Ca/40 nozzle and mould temperature were slightly lower than in the table in Figure 7.1.



Material	1st Zone °C	2nd Zone °C	3rd Zone °C	Nozzle °C	Mould °C
Filled	190-210	200-220	210-230	210-230	50-70
Reinforced	200-220	230-250	220-240	220-240	50-70

Figure 7.1. *Polifor PP plastics injection molding temperatures ranges and zones. Modified from [72]*

Injection molding tests with Fanuc machine were executed with the mold that was modified from a cover mold of an old Nokia mobile phone. The mold has been used in testing of many materials. Therefore, test results are comparable with earlier materials and some facts can immediately be seen from the results. Figure 7.2. illustrates the test pieces that were molded with Fanuc injection molding machine. Furthermore, as well as with ENGEL injection molding machine was used a mold which was modified from a mold from the cover of an old Nokia mobile phone. In Figure 7.3. is illustrated a test piece that was injection molded with ENGEL injection molding machine. The design of cover was minutely simplified when compared to the design of a cover for mobile phone on the market. The pictures of the test pieces in

Figures 7.2. 7.3. and 7.4. were photographed with Nikon D3100 and Nikkor AF-S DX 18-55 mm II lens.

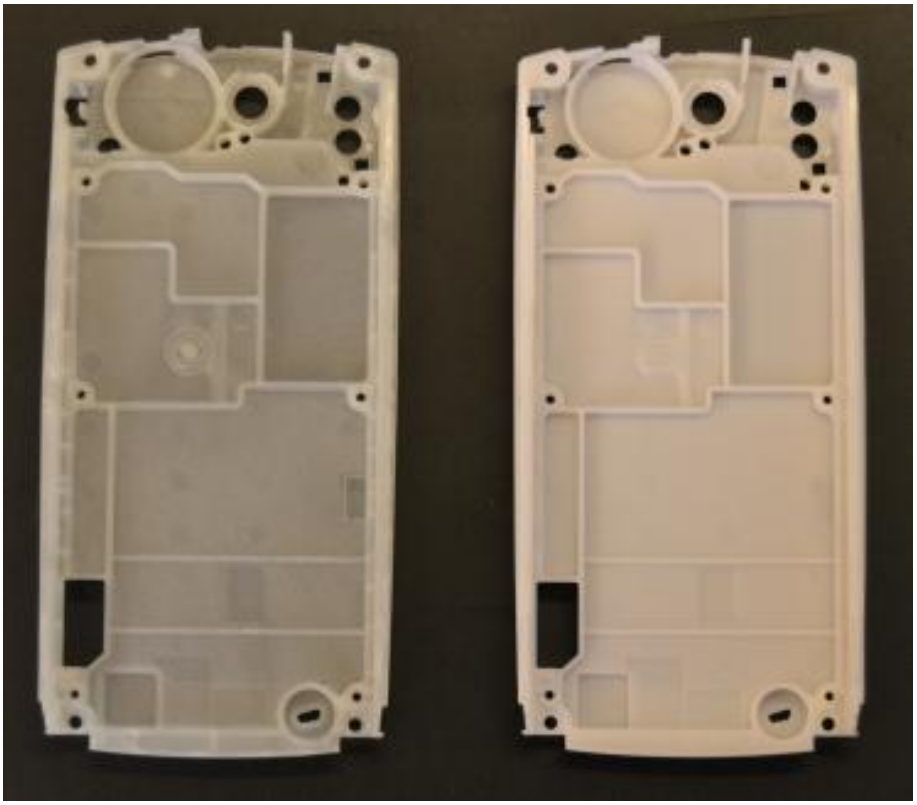


Figure 7.2. *Shape of test pieces molded with Fanuc injection molding machine. On the left is PP GF/30 and on the right is PP Ca/40.*

Figure 7.3. *Shape of test pieces molded with ENGEL injection molding machine.*

With the two PP GF grades there were no problems in injection molding but with the PP Ca/40 grade there was a problem with how products disengaged from ENGEL's mold. The design of the cover included one point that stuck to the mold almost every time and inflicted the product slightly. This small mark can be seen in Figure 7.4.

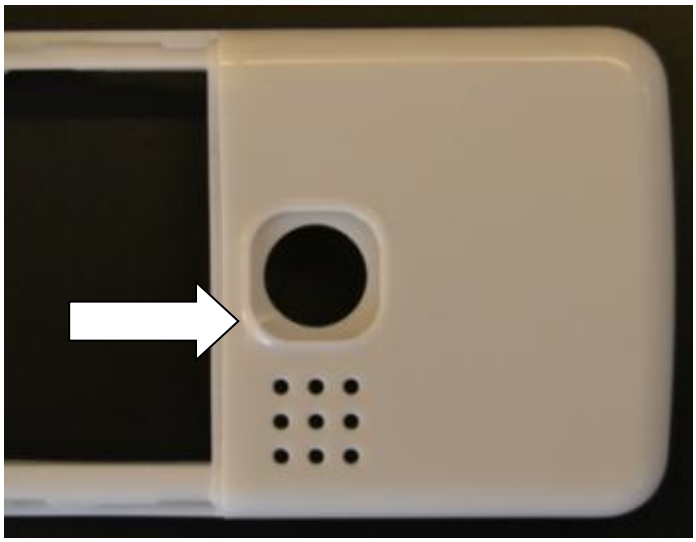


Figure 7.4. *White arrow indicates the small mark that was caused when product disengage from the mold.*

Even before testing some differences between the materials could be observed, with a brief empirical examination of the molded products. As mentioned before, pure polypropylene is an almost transparent material and the two grades that have glass reinforcements were also quite transparent. If an object was placed behind the injection molded cover the object's silhouette was visible through the test piece. The injection molded pieces of the two grades had a very similar appearance and they could only be differentiated on their slight color difference and difference on how light could pass through the plastic. Both of these properties could be because of the difference of the amount of glass fibers. As distinction of PP GF grades of PP Ca/40, manufactured test pieces were white, although the grade was natural thus there were no added colorants. The mineral filler of PP Ca/40 plastic gave the products their white color. The color difference can be seen in Figure 7.2. Another easily notable difference was the difference in toughness of the test pieces. While bending PP GF plastics they broke in the rod-like part. Whereas PP Ca/40 plastic did not break down but simply bended. PP Ca/40 was remarkably tougher. However, PP GF plastics required more force to bend than PP Ca/40 plastic. There was also a difference in surface hardness of test pieces when surfaces were scratched with fingernails or keys. Fingernails did not scratch any of the plastics surfaces, but keys did them all.

7.4. Materials injection moldability tests

The Fanuc injection molding machine was used to test how materials behave when they are injection molded. These tests concentrate on the properties of the plastics rather that how well materials could be used in a specific application. All these were done with test pieces illustrated in Figure 7.2.

7.4.1. Injection speed optimization

Injection speed optimization was done with Fanuc injection molding machine. All molded test pieces were left similarly slightly incomplete. Injection speed was decreased 20 mm/s at a time and exchange point was the same throughout the test. Changes in maximum injection pressure and injection time were observed. From these values a computer drew a peak injection pressure versus injection time curve.

Figure 7.5.illustrates injection pressure versus injection time curves of PP GF/30, PP GF/40 and PP Ca/40. Shapes of the curves and their places in the xy diagram can be compared from Figure 7.5.The shapes of PP GF/30 and PP GF/40 curves are very similar. The curves begin from the highest value and then gradually descend to the lowest value. Whereas the shape of PP Ca/40's curve is different, the curve also begins from the highest value and then descends but in the end it starts to rise. If curve starts to rise in the end, in these injection speeds, the molten plastics may start to crystallize too fast.

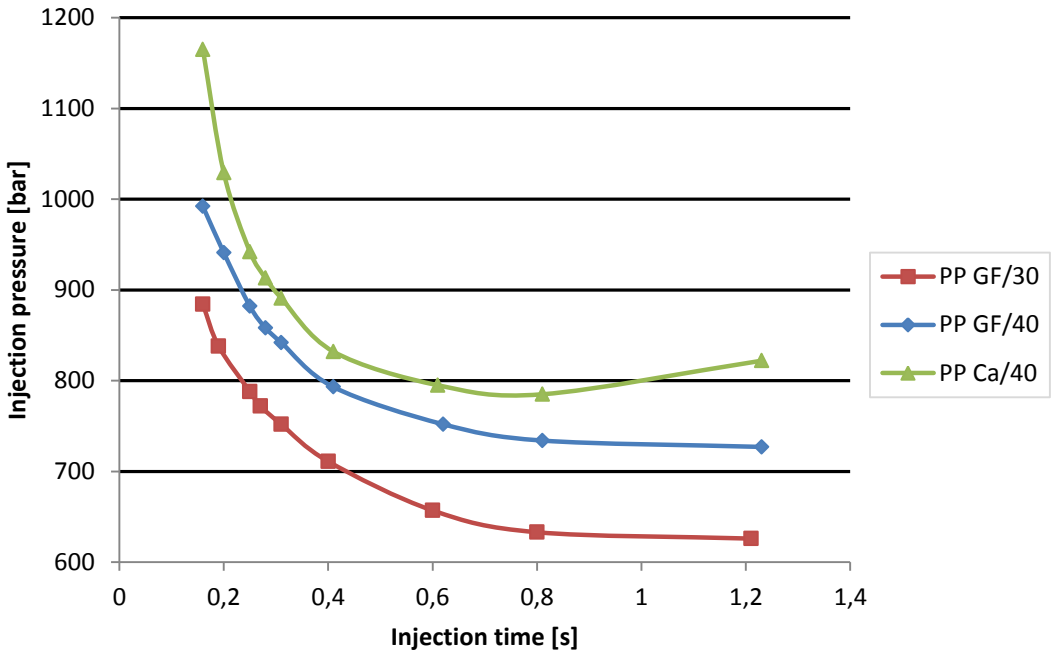


Figure 7.5. *Pressure versus injection time curves of PP GF/30, PP GF/40 and PP Ca/40 plastics.*

Table 7.1. shows the values for Figure 7.5. Using the values in the table it is quite easy to compare how injection pressures of the plastics vary in the same injection time. From Table 7.1. it can be also seen how injection time and maximum injection pressure change when injection speed is altered. PP Ca/40 requires more pressure in fast injection speeds than the two other plastics. When the injection time is 0.16 seconds and injection speed is 160 mm/s injection pressure of PP Ca/40 is 1165 bar while PP GF/40 is 992 bar and PP GF/30 is 884 bar, the difference is almost 300 bar. In the middle of the curves where injection speeds are in normal level the injection pressure differences

are smaller. For example, if injection time is 0.31 seconds and injection speed is 80 mm/s then injection pressures are: PP GF/30 752 bar, PP GF/40 842 bar and PP Ca/40 891 bar. All pressures are within a range of 100 bars. As mentioned before the curve of PP Ca/40 rises in the end, when injection speed level is low, meaning that injection pressure is rising. When injection time is 1.23 seconds and injection speed is 20 mm/s, injection pressures are: PP GF/30 626 bar, PP GF/40 727 bar and PP Ca/40 822 bar. Pressure difference of plastics is again larger. Furthermore, as can be seen from Table 7.1. and Figure 7.5., injection pressure of PP Ca/40 in the end of the curve is larger than in the two last injection speeds whereas PP GF plastics injection pressures descend.

Table 7.1. *Injection speed is altered and observed how maximum injection pressure and injection time are changed.*

		Injection pressure (bar)		
Injection speed (mm/s)	**Injection time (s)**	**PP GF/30**	**PP GF/40**	**PP Ca/40**
160	0.16	884	992	1165
130	0.19*; 0.20	838	941	1029
100	0.25	788	882	942
90	0.27*; 0.28	772	858	913
80	0.31	752	842	891
60	0.40*; 0.41	711	793	832
40	0.60*; 0.61; 0.62**	657	752	795
30	0.80*; 0.81	633	734	785
20	1.21*; 1.23	626	727	822

* PP GF/30 **PP GF/40

7.4.2. Filling pattern

Filling pattern test was done with Fanuc injection molding machine. This test was used to study how molten plastic spread to the molt. The test is essential when Moldflow calculations and realized plastic spread in a mold are compared.

The injection molding of the test was started with a nearly complete product and during the test the completeness of products was decreased in nine steps. So that outcome was ten dissimilar products. With all the products the injection speed was 80 mm/s. The switch over point was altered and changes in injection time and injection pressures were observed. With each of the three plastics the first switch over point was determined from the first product, which was correctly incomplete. The switch over point of the next product was 1.5 mm smaller than previous and this occurred during the whole test with all the products.

Maximum pressure and injection time altered with all products. The amount of pressure indicates how much pressure is needed to spread the molten plastic that far in the mold at that injection time. Injection pressure differences of the plastics, while injection time is altered, are in Table 7.2.

***Table 7.2**. Injection pressures of plastics when injection time is altered.*

	Injection pressure (bar)		
Injection time (s)	**PP GF/30**	**PP GF/40**	**PP Ca/40**
0.31	762	858	888
0.29; 0.30*	729	820	840
0.27; 0.28*	706	795	811
0.25; 0.26*	684	769	776
0.24	663	743	743
0.22	638	718	700
0.20	615	692	663
0.18; 0.19*	594	667	628
0.16; 0.17*	568	637	596
0.14; 0.15*	528	599	557

* PP GF/40

7.4.3. Flatness and shrinkage

Warpage of a plastic product is measured with flatness. In this case flatness was measured by Smartscope Zip250 (No. SK2501458) machine with MeasureMind® software and measurements were controlled with a computer. The flatness measurement was done with the measurement tool because of the differences in flatness were so small. Before the test pieces of the semi-crystalline PP plastics could be measured reliably they needed to settle down for 24 hours because of their shrinking.

The test pieces, from which flatness were measured, were injection molded with Fanuc injection molding machine and their shape was the same as in earlier tests. The test pieces were injection molded with three different holding pressures: 400, 600 and 800 bar. There were ten duplicate test pieces for every pressure for all of the three PP plastics. The flatness measurement was done with six measurement points; their positions are illustrated in Figure 7.6. All the six points are placed so that they represent an attachment point to a technical part such as a screw of a circuit board.

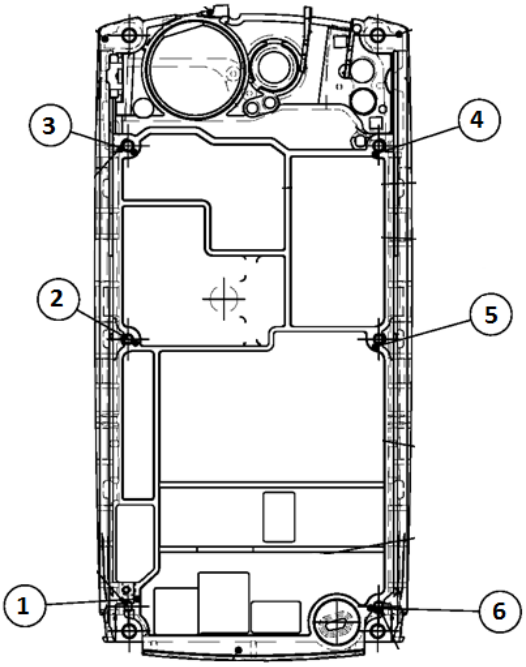


***Figure 7.6**. Flatness six measuring points.*

From the six points of interest the Smartscope Zip250 measures the z-axis difference of the point to the axis zero level. The difference could be downward negative or upward positive. In Table 7.3. are flatness values of the measurement points for holding pressure 600 bar. The values are averaged of the ten test pieces at the same holding pressure. According to the six measuring points values a computer calculates total flatness of the test pieces.

***Table 7.3.** The z-axis values of the measurement points and total flatness.*

	PP GF/40 (mm)	PP GF/30 (mm)	PP CA/40 (mm)
1	0.12	0.02	-0.23
2	0.05	0.19	0.22
3	-0.16	-0.18	0.00
4	0.10	0.03	-0.18
5	0.04	0.14	0.08
6	-0.15	-0.15	0.10
Total flatness	0.37	0.27	0.45

In this case the desired value for flatness is less than 0.30 mm and it is used as a limit value. The limit comes from requirements of Nokia. The desired flatness is dependent on design and size of the part. From the tested plastics only flatness of PP GF/30, 0.27 mm, was under and PP GF/40 value 0.37 mm was slightly over the limit. Flatness of PP Ca/40 is quite poor with 0.45 mm. The smaller the total flatness values are the smaller the warpage of the product, hence the products are flatter. When a

product is flat it is better for the technical components because they cannot endure distortion.

With the same measurement tool Smartscope Zip250 it was also measured how test pieces shrink to x- and y-axis directions. X-y shrinkage values to these PP plastics are shown in Table 7.4. X-y shrinkage is calculated using x-axis shrinkage minus y-axis shrinkage. So that if the x-y shrinkage value is negative, a product has shrank more in y-axis direction than the x-axis direction. When looking at the sketch in Figure 7.6. x-axis is horizontally and y-axis is vertically. X-y shrinkage is a property of the plastic. To amorphous plastics shrinkage is usually isotropic and this value is close to zero, while plastic shrinks equally to both x- and y-axes direction. On the other hand crystalline and semi-crystalline plastics shrink unequally to x- and y-axes direction. Therefore, x-y shrinkage of these plastics is usually larger than that of amorphous plastics.

Table 7.4. *Shrink X – Shrink Y values of PP GF/30, PP GF/40 and PP Ca/40 plastics.*

	PP GF/30	PP GF/40	PP Ca/40
Shrink X - Shrink Y	0.07	0.09	-0.06

7.4.4. Flash

Flashes of the plastics were also observed with Smartscope Zip250. Flash is a material that is flown into clearances of parting line, central core or ejection mechanism. Flash could be caused because the mold is not tight enough, clamping force of machines is not high enough, inner pressure of the mold is too high or molten material viscosity is too low. [73] All plastic materials flash to some extent but the amount of flash is dependent on the properties of plastic such as how well molten plastic flows [36]. The flashes were examined from the same test pieces as flatness whose holding pressure was 800 bar, from the right hand bottom corner. The flashes of the PP plastics were not visually perceptible. The flashes of the tested plastics are in Figure 7.7.

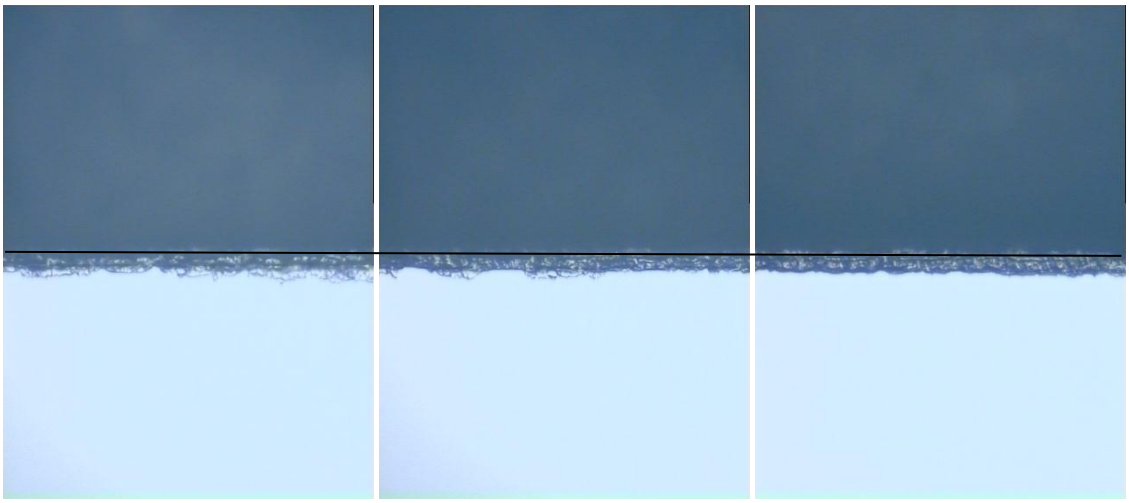


Figure 7.7. *Flashes of the plastics, on the left hand side is PP GF/30, in the middle is PP GF/40 and on the right hand side is PP Ca/40. A black line indicates where edge of the part is.*

Figure 7.7. also shows some differences in the PP plastics. The pictures of PP GF/30 and PP GF/40 are very similar while some glass fibers can be seen at the edges of the material. When these pictures are compared to picture of PP Ca/40 it can be seen that there are no fibers as the outer edge of the material is neat. Some small particles can also be seen in the PP Ca/40 plastic.

7.5. Discussion

After injection speed optimization of GF/30, PP GF/40 and PP Ca/40 plastics it can be said that all three grades would suit injection molded cover parts of mobile phones. When injection pressure vs. injection time curve of PP Ca/40 was noticed, it was considered if the mineral filler of the plastic could affect crystallization and cause elevation of the curve in the slower injection speeds. It was considered that the mineral filler particles could function as crystal nucleus and offer starting points for crystallization.

Despite some small problems with PP Ca/40 plastic with Engel injection molding machine injection molding process stability and mold release of all three PP plastics were evaluated as perfect using the following scale Perfect – OK – Some issues – Poor.

Flatness values of the tested PP plastic were not that good and in fact only PP GF/40 flatness was under the 0.3 limit while the two plastics flatness values were PP GF/30 0.37 and PP Ca/40 0.45. For comparison flatness of one of the ABS+PC plastics is 0.184. Flatness values vary significantly even with plastics of the same polymer. Polymer of the plastic, filler or reinforcement and its shape affects flatness. Furthermore, flatness values of the tested plastic may be improved together with the manufacturer by changing shape, size of filler or reinforcement or type of the polymer.

PP Ca/40 had also some rather unexpected behavior as its shrinkage in flow direction was larger than in a direction transverse to flow. When comparing x-y-shrinkage with values, as stated before the shrinkage of the PP plastics were: GF/30 0.07, GF/40 0.09 and Ca/40 -0.06, whereas x-y shrinkage of one ABS+PC plastic is 0.01. Shrinkage is one of the properties of the PP plastic, so it cannot be prevented entirely by improving or altering structure or composition of plastics. When the shrinkage is known, injection molding molds can be designed according to it.

The flashes of all the three tested PP plastics were at good level and they are similar to low flash materials. The flashes of the PP plastics were at the same level as flash of a currently utilized ABS+PC plastic, that flash quite little. Furthermore, the filling pattern test was done merely so that the realized melt flow could be compared with Moldflow calculations.

8. CONCLUSION

The main goal for this thesis was to evaluate if PP plastics could be utilized in covers of mobile phones. Other goals were to compare sustainability of polypropylene to sustainability of other plastics, surveying biopolypropylene as an alternate option, as well as market and industry trends of polypropylene.

In the LCA study polypropylene was evaluated as more sustainable than other plastics used in the test. However, in an application like a mobile phone, plastics need to be selected also according to their mechanical properties. After the literature survey it was clear that properties of polypropylene were not at the same level as the utilized engineering plastics. However, the mechanical properties of the PP plastics with reinforcements were better than pure PP plastics.

When plastics were selected for the injection moldability test they were selected according to reference materials. The mechanical properties of these reference materials were so advanced that pure PP plastics did not achieve them. Therefore, none of the tested plastics were pure PP plastic.

As the injection moldability tests showed, one of the tested plastics, PP GF/30, would be directly suitable for mobile phone plastic parts using injection molding manufacturing in tested-like molds. The other two plastics would also suit injection molding in tested-like molds. However, their warping in tested parts was too large. The warping of the plastics might be improved if the plastics would be developed with the manufacturer.

Although PP plastics appear promising according to results some further studies need to be performed before any decisions of PP plastics use in certain parts of mobile phones could be done.

9. SUGGESTIONS FOR FUTURE STUDIES

Before the tested PP plastics suitability to mobile phone material can be confirmed, test pieces need to be tested further. These tests would be performed with ENGEL injection molded test pieces. Necessary tests are for instance: UV stability, temperature, drop and chemical resistance against some common everyday substances. Needed tests are from requirements of Nokia for their products.

Surface quality of the tested plastics was hard to evaluate, because the plastics were natural grades. Therefore, surface quality of plastics would need to be tested with colored plastics.

It would also be interesting to know if PP plastics with natural fiber reinforcements would be suitable for this kind of injection molding and how the injection molding parameters and injection moldability test results would differ from results of conventional PP composites and presently utilized plastics. Furthermore, their properties would need to be tested further, if their suitability for mobile phone application are to be solved.

Additionally, improvement of biopolypropylene needs to be observed for some time. It could offer a sustainable option for conventional plastics, if manufactured from sustainable sources.

REFERENCES

[1] Alperowicz, N. Polypropylene Versatile Drives Growth. Chemical Week Magazine - Companies. [WWW newspaper]. October 18, 2010. [Cited 26.10.2010] Restricted access: www.chemweek.com/sections/companies/30266.html

[2] Arranz-Andrés, J., Peña, B., Benavente, R., Pérez, E. & Cerrada, M. L. Influence of isotacticity and molecular weight on the properties of metallocenic isotactic polypropylene. European Polymer Journal 43(2007)6, pp. 2357-2370. DOI 10.1016/j.eurpolymj.2007.03.034.

[3] Burkhardt, G., Hüsgen, U., Kalwa, M., Pötsch, G. and Schwenzer, C. Plastics, Processing. In: Ullmann's Encyclopedia of Industrial Chemistry. 2000. Wiley-VCH Verlag GmbH & Co. KGaA. DOI: 10.1002/14356007.a20_663. ISBN: 9783527306732

[4] Busico V. & Cipullo R. Microstructure of polypropylene. Progress in Polymer Science 26(2001)3, pp. 443-533.

[5] Calhoun, A. Polypropylene In: Wagner, J. R. Jr. (ed.). Multilayer Flexible Packaging. 2009. Elsevier Inc. pp. 31-36. ISBN 978-0-8155-2021-4.

[6] Callister, W. D. Jr. Materials Science and Engineering an Introduction. 6TH Edition. USA 2003, John Wiley & Sons, Inc. 820+21 p. ISBN 0-471-22471-5.

[7] Cherubini, F. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management 51(2010)7, pp. 1412-1421. DOI 10.1016/j.enconman.2010.01.015.

[8] Cherubini, F. & Ulgiati S. Crop residues as raw materials for biorefinery – A LCA case study. Applied Energy 87(2010)1, pp. 47-57. DOI 10.1016/j.apenergy.2009.08.24.

[9] Forsblom, S. A framework for designing the ecoprofiles of mobile devices. Master of Science Thesis. Helsinki 2008. Helsinki University of Technology, Department of Civil and Environmental Engineering, Laboratory of Environmental Protection. 97+58 p.

[10] Fried, J. R. Polymer Science & Technology, 2ND Edition. USA 2003, Pearson Education, Inc. 582+17 p. ISBN 0130181684.

[11] Harlin, A., Edelmann, K., Immonen, K., Mroueh, U-M., Pingoud, K. & Wessman, H. Industrial Biomaterial Visions. 2009, VTT, VTT Tiedotteita - Research Notes 2522. 87 p.

[12] Hart, H., Craine, L. E. & Hart, D. J. 2003. Organic Chemistry a short course. 11TH Edition. USA 2003, Houghton Mifflin Company. 566+24 p. ISBN 0-618-215360.

[13] Hartikainen, J., Hine, P., Szabó, J.S., Lindner, M., Harmia, T., Duckett, R.A. & Friedrich, K. Polypropylene hybrid composites reinforced with long glass fibers and particulate filler. Composites Science and Technology 65(2005)2, pp. 257-267. DOI 10.1016/j.compscitech.2004.07.010.

[14] Hristov, V. N., Lach, R. & Grellmann W. Impact fracture behavior of modified polypropylene/wood fiber composites. Polymer Testing 23(2004)5, pp. 581-589. DOI 0.1016/j.polymertesting.2003.10.011.

[15] http://archive.greenpeace.org/toxics/pvcdatabase/bad.html [WWW]. [Cited 12.10.2010]

[16] http://cereplast.com/datasheets/HybridPropertyGuides/Hybrid%20103%20Property%20Guide%20-%20High%20Melt%20Flow%20Injection%20Molding.pdf [Data sheet]. [Cited 2.3.2011]

[17] http://en.wikipedia.org/wiki/File:Spherulite2.PNG [WWW]. [Retrieved 14.2.2011]

[18] http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf [WWW]. [Cited 18.1.2011]

[19] http://monographs.iarc.fr/ENG/Classification/index.php [WWW]. [Cited 18.1.2011]

[20] http://nds1.nokia.com/eco_declaration/files/eco_declaration_phones/C7-00_Eco_profile.pdf [WWW]. [Cited 10.2.2011]

[21] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:026:0011:0014:FI:PDF [Directive]. [Cited 29.3.2011] In Finnish only

[22] Höök, T. & Nykänen, S. ValuAtlas – Kestomuottivalun suunnittelu. 1999. [Cited 23.3.2011]. Available: http://www.valuatlas.net. In Finnish only

[23] ISO 14040:2006. Environmental management – Life cycle assessment – Principles and framework. 2006, British Standards Institution BSI. 32+6 p.

[24] ISO 14044:2006. Environmental management – Life cycle assessment – Requirements and guidelines. 2006, British Standards Institution BSI. 46+6 p.

[25] Järvinen, P. Uusi muovitieto. Porvoo Finland 2008, Muovifakta Oy. WS Bookwell Oy. ISBN 978-952-92-3558-2. 263 p. In Finnish.

[26] Kamm, B. & Kamm, M. Principles of Biorefineries. Applied Microbiology and Biotechnology 64(2004)2, pp. 137-145.

[27] Karmarkar, A., Chauhan, S. S., Modak, J. M. & Chanda, M. Mechanical properties of wood-fiber reinforced polypropylene composites: Effect of a novel compatibilizer with isocyanate functional group. Composites: Part A applied science and manufacturing 38(2007)2, pp. 227-233 DOI 10.1016/j.compositesa.2006.05.005.

[28] Keener, T. J., Stuart, R. K. and Brown T. K. Maleated coupling agents for natural fibre composites. Composites: Part A applies science and manufacturing 35(2004)3, pp. 357-362.

[29] Khalid, M., Ratnam, C. T., Chuah, T. G., Ali, S. & Choong, T. S. Y. Comparative study of polypropylene composites reinforced with oil palm empty fruit bunch fiber and oil palm derived cellulose. Materials and Designs 29(2008)1, pp. 173-178. DOI 10.1016/j.matdes.2006.11.02.

[30] Lebo S. E. Jr., Gargulak J. D. & Mcnally T. J. Lignin In: Kirk-Othmer Encyclopedia of Chemical Technology. 2001. John Wiley & Sons, Inc.

[31] Mair R. D. Polypropylene: Metallocene-Based Isotactic In: Buschow, K. H. J., Cahn, R., Flemings, M., Ilschner, B., Kramer, E., Mahajan, S. & Veyssiere, P. (ed.). Encyclopedia of Materials: Science and Technology. 2001, Elsevier Science Ltd. pp. 7698-7700. ISBN 978-0-08-043152-9.

[32] Maier, C. & Calafut, T. Polypropylene - The Definitive User's Guide and Databook. 1998, Plastic Design Library, William Andrew Inc. 413+20 p. ISBN 1-884207-58-8.

[33] Qiu, W., Endo, T. and Hirotsu, T. Structure and properties of composites of highly crystalline cellulose with polypropylene: Effects of polypropylene molecular weight. European Polymer Journal 42(2006)5, pp. 1059-1068. DOI 10.1016/j.eurpolymj.2005.11.012.

[34] Rockey, B. Injection Molding Machine. 2009. [WWW]. [Retrieved 2.2.2011] Available: http://en.wikipedia.org/wiki/File:Injection_molding.png

[35] Sannigrahi, P., Pu, Y. & Ragauskas, A. Cellulosic biorefineries – unleashing lignin opportunities. Current Opinion in Environmental Sustainability 2(2010)5-6, pp. 383-393. DOI 10.1016/j.cosust.2010.09.004.

[36] Silvennoinen, Mikko. 2011, Lite-On Mobile/Perlos. Email conversation.

[37] Song, J. H., Murphy, R. J., Narayan, R. & Davies, G. B. H. Biodegradable and compostable alternatives to conventional plastics. Philosophical Transactions B 364(2009) pp. 2127-2139. The Royal Society. DOI 10.1098/rstb.2008.0289.

[38] Tabone, M. D., Cregg, J. J., Beckman, E. J. & Landis, A. E. Sustainability Metrics: Life Cycle Assessment and Green Design in Polymer. Environmental Science Technology 44(2010)21, pp. 8264-8269.

[39] Takayama, Shin. Environmental Specialist - Materials, Nokia Corporation. Tampere. Discussion 4.11.2010.

[40] Takayama, Shin. 2011, Environmental Specialist - Materials, Nokia Corporation. Email conversation.

[41] Vauhkonen, Sami. Manager - Material technology, Lite-On Mobile/Perlos. Vantaa. Discussion 9.3.2011.

[42] www.biotimes.com/en/Articles/2010/June/Pages/Partnershiptoturnsugarintoplastic.aspx [Article]. [Cited 28.10.2010]

[43] www.borealisgroup.com/ [WWW]. [Cited 17.2.2011]

[44] www.borealisgroup.com/news-and-events/product-news/archive-2011/20110112Peugeotfrontgrill [Press release]. [Cited 13.1.2011]

[45] www.braskem.com.br/site/portal_braskem/en/sala_de_imprensa/sala_de_imprensa_detalhes_10415.aspx [Press Release]. [Cited 9.11.2010]

[46] www.braskem.com/plasticoverde/EN_HOME.html [WWW]. [Cited 28.10.2010]

[47] www.braskem.com/plasticoverde/EN_Research.html [WWW]. [Cited 4.11.2010]

[48] www.campusplastics.com [Database]. [Cited 15.11.2010]

[49] www.cas.org/expertise/cascontent/registry/regsys.html [WWW]. [Cited 18.1.2011]

[50] www.cereplast.com/cmspage.php?pgid=68 [WWW]. [Cited 29.3.2011]

[51] www.cereplast.com/cmspage.php?pgid=71 [WWW]. [Cited 27.10.2010]

[52] www.chemsystems.com/reports/search/docs/abstracts/0708S11_abs.pdf [Report Abstract]. [Cited 6.4.2011]

[53] www.curvonline.com [WWW]. [Cited 28.10.2010]

[54] www.ecoinvent.org [Database]. [Cited 28.10.2010]

[55] www.eea.europa.eu [WWW Glossary]. [Cited 24.11.2010]

[56] www.exxonmobil.com/Corporate/default.aspx [WWW]. [Cited 17.2.2011]

[57] www.gabi-software.com [WWW]. [Cited 23.2.2011]

[58] www.icis.com/v2/chemicals/9076455/propylene/uses.html [WWW]. [Cited 26.10.2010]

[59] www.kareline.fi/en/main+page [WWW] [Cited 26.10.2010]

[60] www.lme.com/dataprices.asp [WWW]. [Cited 21.12.2010] [Figures retrieved 1.4.2011]

[61] www.lyondellbasell.com/index.htm [WWW]. [Cited 17.2.2011]

[62] www.materialdatacenter.com [Database]. [Cited 18.11.2010]

[63] www.matweb.com [Database]. [Cited 18.11.2010]

[64] www.nokia.com/ecoprofile [WWW]. [Cited 10.2.2011]

[65] www.nokia.com/lca [WWW]. [Cited 12.10.2010]. [Figures retrieved 14.2.2011]

[66] www.nokia.com/lct [WWW]. [Cited 12.10.2010]

[67] www.nokia.com/materials [WWW]. [Cited 30.11.2010]

[68] www.pre.nl/download/manuals/DatabaseManualMethods.pdf [Manual]. [Cited 24.11.2010]

[69] www.pre.nl/download/manuals/SimaPro7IntroductionToLCA.pdf [Manual]. [Cited 24.11.2010]

[70] www.pre.nl/eco-indicator99 [WWW]. [Cited 2.11.2010]

[71] www.softerspa.com/en/products/Engineering-Thermoplastics/Polifor%20/details?productid=27&macrode=Engineering-Thermoplastics&prdName=Polifor [WWW]. [Cited 11.3.2011]

[72] www.softerspa.com/uploads/VW/_m/VW_m4HmKJRaGzmuaDZygmA/POLIFOR-09-2009.pdf [Brochure]. [Cited 16.3.2011]

[73] www.tut.fi/plastics/tyreschool/tuula/Ruiskuvalu/suomi/sanasto/index.html [Glossary]. [Cited 21.3.2011] In Finnish

[74] Xu, X., Jayaraman, K., Morin, C. & Pecqueux N. Life cycle assessment of wood-fibre-reinforced polypropylene composites. Journal of Material Processing Technology 198(2008)1-3, pp. 168-177. DOI 10.1016/j.jmatprotec.2007.06.087.

[75] Yamaguchi, M., Irie, Y., Phulkerd, P., Hagihara, H., Hirayama, S. & Sasaki, S. Plywood-like structure of injection-moulded polypropylene. Polymer 51(2010)25, pp. 5983-5989. DOI 10.1016/j.polymer.2010.10.007.